Department of Process and Environmental Engineering

Mass and Heat Transfer Process Laboratory

Diploma thesis

Feasibility study and sustainability assessment for selected CO_2 utilizing reaction routes

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Author:

_____

Matti Kinnula

Supervisor:

_____

Riitta Keiski

Professor

Advisors:

_____

Mika Huuhtanen

D. Sc (Tech)

_____

Paula Saavalainen

M. Sc. (Chem.)

_____

Esa Turpeinen

M. Sc. (Eng.)

UNIVERSITY OF OULU   Thesis Abstract

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Author	Thesis Supervisor
Kinnula Matti Kossi	Keiski R. Professor

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Feasibility study and sustainability assessment for selected CO_2 utilizing reaction routes

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Abstract

The purpose of the thesis was to evaluate the feasibility and sustainability of selected CO_2 utilizing reaction routes. The literature part included the chemical properties, sources and legislation of CO_2. CO_2 capture methods were gathered and reviewed concentrating on the post-combustion capture. Industrial applications of CO_2 utilization were summarized. Three selected conventional route vs. CO_2 utilizing route pairs were reviewed: syngas production via steam methane reforming (SMR) vs. dry reforming, syngas based methanol synthesis vs. methanol synthesis using CO_2 and dimethylcarbonate (DMC) production via oxidative carbonylation vs. direct synthesis of DMC via CO_2. The process technology of each route was reviewed concentrating on reactors and catalysts and their further development research. Also sustainability assessment as a tool for engineers is reviewed in the literature part.

Feasibility study consisted of thermodynamic and economic studies. Thermodynamic calculations were simulated with HSC Chemistry (syngas and methanol cases) and Aspen Plus (DMC case). Different CO_2 tax costs and CO_2 separation costs were used to evaluate the costs of the conventional process and the CO_2 utilizing process. Facts and assumptions of each process were gathered for the sustainability assessment questionnaire. The questionnaire based on 12 principles of Green Chemistry consists of questions concerning environmental, social and economic impacts of the processes.

Dry reforming was found to be a slightly more sustainable process than SMR but it had a lower economic competence. Methanol synthesis via syngas performed better in both feasibility and sustainability. DMC production via oxidative carbonylation was cheaper than the CO_2 route but the CO_2 route was more sustainable. Chemical utilization of CO_2 was claimed as a promising way in certain cases to have use for captured CO_2. The suggestion was that further research on the subject should concentrate on laboratory scale tests and more complex process simulations.

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Additional Information

OULUN YLIOPISTO   Tiivistelmä opinnäytetyöstä

Teknillinen tiedekunta

Osasto	Pääopintojen ala
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Työn nimi			
Käyttökelpoisuus- ja kestävyystarkastelu valituille hiilidioksidia hyötykäyttäville reaktioreiteille			

Oppiaine	Työn laji	Aika	Sivumäärä
Tuotantoteknologia	Diplomityö		105s., 18s., 3 liitettä.

Tiivistelmä

Työn tavoitteena oli arvioida valittujen hiilidioksidia (CO_2) kemiallisesti hyödyntävien reaktioreittien käyttökelpoisuutta ja kestävyyttä. Kirjallisuusosiossa tarkasteltiin CO_2:n kemiallisia ominaisuuksia, lähteitä sekä CO_2-päästöjä koskevaa lainsäädäntöä. Hiilidioksidin erotusmenetelmiä tarkastellaan polton jälkeiseen erotukseen keskittyen. Teollisesti käytössä olevat hiilidioksidin hyödyntämiskohteet esitellään myös. Kolme valittua kemiallisesti hiilidioksidia hyötykäyttävää reaktioreittiä sekä niiden vastaavat konventionaaliset reitit tarkastellaan yksityiskohtaisemmin. Valitut parit olivat höyryreformointi – kuivareformointi, synteesikaasupohjainen metanolisynteesi – metanolisynteesi hiilidioksidin avulla sekä dimetyylikarbonaatin (DMC) valmistus karbonylointi reaktiolla – DMC:n valmistus suoraan CO_2-synteesillä. Reittien prosessiteknologia ja teknologian kehityskohteet käydään läpi keskittyen reaktoreihin ja katalyytteihin. Kirjallisuusosion lopuksi esitellään kestävyyden arvioimismetodeja insinöörityökaluna.

Prosessin käyttökelpoisuuden tutkinta sisältää termodynaamisen sekä taloudellisen laskennan. Termodynaamiset tarkastelut tehtiin HSC Chemistryllä (reformointi- sekä metanolicaset) ja Aspen Plus:lla (DMC case). Termodynaamisista tutkimuksista saadut aine- ja energiataseet olivat perusta taloudellisille tarkasteluille. CO_2:a hyötykäyttävän reitin sekä konventionaalisen reitin kustannuksia tarkasteltiin eri CO_2-veroilla sekä CO_2-erotuskustannuksilla. Kestävyysarviointi tehtiin kysymyslistalla kullekin prosessille faktojen ja oletusten pohjalta. Kysymyslista pohjautuu vihreän kemian 12 periaatteeseen sisältäen kysymyksiä prosessin ympäristöllisiin, sosiallisiin sekä taloudellisiin vaikutuksiin.

Kuivareformointi todettiin kestävyyden kannalta höyryreformointia paremmaksi prosessiksi, mutta taloudellisesti ei yhtä kannattavaksi. Synteesikaasupohjainen metanolisynteesi osoittautui paremmaksi kuin CO_2-reitti sekä kannattavuudeltaan että kestävyydeltään. DMC:n valmistus karbonylaatioreitillä on halvempaa, mutta kestävyydeltään se on haitallisempi. CO_2:n kemiallinen hyötykäyttö todettiin lupaavaksi keinoksi hyödyntää savukaasuista erotettu CO_2. Jatkotutkimusaiheiksi ehdotettiin laboratoriotestejä CO_2-reittien katalyysi- ja reaktoritutkimukseen sekä laajempia tietokonesimulointeja.

Säilytyspaikka
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Muita tietoja

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Abbreviations

aq	Aqueous
C_p	Heat capacity at constant pressure
CCS	Carbon capture and storage
CLC	Chemical looping combustion
EOR	Enhanced oil recovery
EU	European Union
EU ETS	EU Emissions Trading System
g	Gas
ΔG°_r	Gibbs free energy
GHG	Greenhousegas
HT	High-Temperature
ΔH°_r	Entalphy
IGCC	Integrated gasification combine cycle
kg	Kilogram
kJ	Kilojoule
kmol	Kilomole
kt	Kilotonne
kWh	Kilowatt hour
l	Liquid
MJ	Megajoule
Mt	Megatonne
MCM-41	Type of an amine enriched sorbent
MCO_3	Metal carbonate
MEA	Monoethanolamine
MPa	Megapascal
MTBE	Methyl tert-buthyl ether
MWh	Megawatt hour
NGCC	Natrium gas-fired combined cycle
PSA	Pressure-Swing Adsorption
S°_r	Entropy
SMR	Steam methane reforming
Syngas	Synthetic gas

Chemical compounds

Ac	Acetate
Ag	Silver
Al_2O_3	Aluminium oxide
Au	Gold
B	Boron
Bis-A	Bisphenol-A
$Bu_2Sn(OMe)_2$	Dibutyltindimethoxide
C	Carbon
$(CH_3O)_2CO$	Dimethylcarbonate
$Ca(OH)_2$	Calcium hydroxide
$CaCO_3$	Calcium carbonate
CaO	Calsium oxide
CeO_2	Cerium oxide
Ce-Ti-O	Cerium titanium oxide
CH_2O	Formaldehyde
CH_3Cl	Chloromethane
CH_3OH	Methanol
CH_4	Methane
Cl	Chloride
$ClCOOCH_3$	Methylchloroformate
CO	Carbon monoxide
Co	Cobalt
CoO	Cobalt oxide
CO_2	Carbon dioxide
CO_3^{2-}	Carbonate group
$COCl_2$	Phosgene
Cr_2O_3	Chronium oxide
CS_2	Carbon disulphide
Cu	Copper
CuO	Copper oxide
DCC	Dicyclohexal carbodiimide
DEA	Diethanolamine
DMC	Dimethylcarbonate
Ga	Gallium
H_2	Hydrogen
H_2NCONH_2	Urea
H_2O	Water
H_2S	Hydrogen sulphide
HCO_3^-	Hydrogen carbonate
HCN	Hydrogen cyanide
HCOOH	Formic acid
HPO_4	Hydrogen phosphate
Ir	Iridium
KOH	Potassium hydroxide
MCM-41	Mobil composition of matter number 41
Me	Metal compound
$MgCO_3$	Magnesium carbonate
MgO	Magnesium oxide
M_2SiO_4	Alkaline earth orthosilicates

MDEA	Methyldiethanolamine
Mo_2C	Molybdenum carbide
NaCl	Natrium chloride
Na_2CO_3	Sodium carbonate
$NaHCO_3$	Sodium bicarbonate
NaOH	Sodium hydroxide
Nb	Niobium
$NdCoO_3$	Perovskite
Ni	Nickel
NiO	Nickel oxide
NO	Nitrogen oxide
NO_2	Nitrogen dioxide
NO	Nitrogen oxide
OAc	Acetate
PC	Polycarbonate
PCC	Precipitated calciumcarbonate
Pd	Palladium
PO_4	Phosphate
Pt	Platinum
Rh	Rhodium
Ru	Ruthenium
SiC	Silicon carbide
$Si(OMe)^4$	Orthoacetate
SiO_2	Silicon dioxide
SO	Sulphate
SO_2	Sulphur dioxide
SO_3	Sulphur trioxide
Ti	Titanium
TiO_2	Titanium dioxide
V	Vanadium
V_2O_5	Vanadium pentoxide
W	Tungsten
WC	Tungsten carbide
Zn	Zinc
ZnO	Zinc oxide
ZrO_2	Zirconium dioxide

Literature part

1   Introduction

There is a common scientific consensus in the world that the increased greenhouse gas emissions cause an effect known as global warming. Most of the impact of greenhouse gases is due the CO_2 emissions. Therefore political decisions have been made to control the amount of CO_2 emissions in atmosphere. Global emission trade has already started (2005 in EU) and the cost of one carbon dioxide ton emitted is increasing all the time.

One method to lower carbon dioxide emissions is carbon capture and storage (CCS). CCS is a way of capturing CO_2 from the emission source and storing it e.g. into old oil or gas spills. Possibilities of chemical utilization of CO_2 are a part of CCS. In the future some natural and fossil fuel based resources could become very scarce. Synthetic chemicals produced from carbon dioxide could replace virgin materials that are running out of the earth.

The aim of the literature part was to study the chemical utilization of CO_2 on general level. Three cases of a conventional process vs. CO_2 utilizing process were selected and reviewed in the literature part. Selected cases were methane steam reforming vs. dry reforming, methanol synthesis vs. methanol synthesis via CO_2 and dimethyl carbonate (DMC) production via oxidative carbonylation vs. direct synthesis of DMC via CO_2. Chapters 5, 6 and 7 describe process technology reviews of the selected CO_2 utilizing reaction routes and their corresponding conventional reaction routes in a more detailed form. The aim of the empirical part was to do a feasibility study and a sustainability studies for the selected CO_2 utilizing reaction routes and compare the results to the corresponding conventional processes.

2 Properties of carbon dioxide

2.1 Chemical properties of carbon dioxide

Carbon dioxide is slightly toxic (in high concentrations), odourless and colourless gas that does not burn or support combustion. It can be utilized in gaseous, liquid or solid forms (Koljonen et al. 2002). CO_2 sublimates at -78 °C which makes it usable for example in icing of e.g. food products. Table 1 shows the properties of CO_2 at atmospheric temperature and pressure. (AGA 2010)

Table 1. Properties of CO_2 in atmospheric conditions (Seppänen et al. 1991).

Molar mass	44.01 g/mol
Phase	Odourless gas
Density	1.977 g/l
Melting point	− 78 °C
Boiling point	− 57 °C
Viscocity	13.6×10^{-6} Ns/m^2
Thermal conductivity	0.015 W/(mK)
Solubility to water	0.88 l/l

As seen from Table 1, solubility of CO_2 into water is 0.88 l/l. This means that at low pressures CO_2 is solved easily into water. Liquid CO_2 can act as a solvent for many reactions. Especially supercritical CO_2 has good properties as a solvent. Figure 1 shows the phase diagram of CO_2 with the triple point and the critical point. (Gassiot 2007)
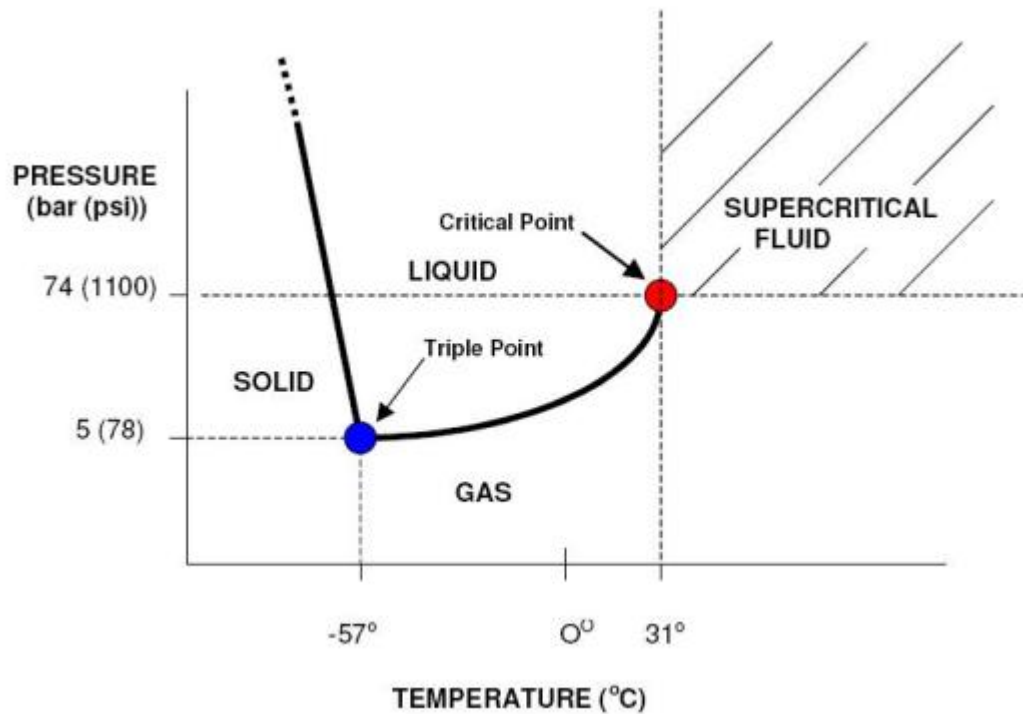
Figure 1. Phase diagram of CO_2 (Gassiot 2007).

As shown in Figure 1, at atmospheric conditions CO_2 is gaseous. The melting point of solid carbon dioxide at 1 bar pressure is - 78 °C. Carbon dioxide can be in liquid phase only above pressures of 5.2 bar. The supercrical fluid area begins at the pressure of 72.9 bar and temperature of 31.3 °C. (Gassiot 2007)

2.2 Sources of carbon dioxide

Atmospheric air consists of only 0.05% of CO_2. Better sources for separation are however available. CO_2 can be extracted from some natural wells. Some captured and separated industrial flue gases contain rather pure CO_2. A typical example is the flue gas from urea synthesis. The growth of fossil fuel based energy consumption and the rise of CO_2-emissions are parallel with each other. This is presented also in Figures 2 and 3. Figure 2 shows the electricity generation by its source. (Aresta 2006, 1, Song 2006, IEA 2009).
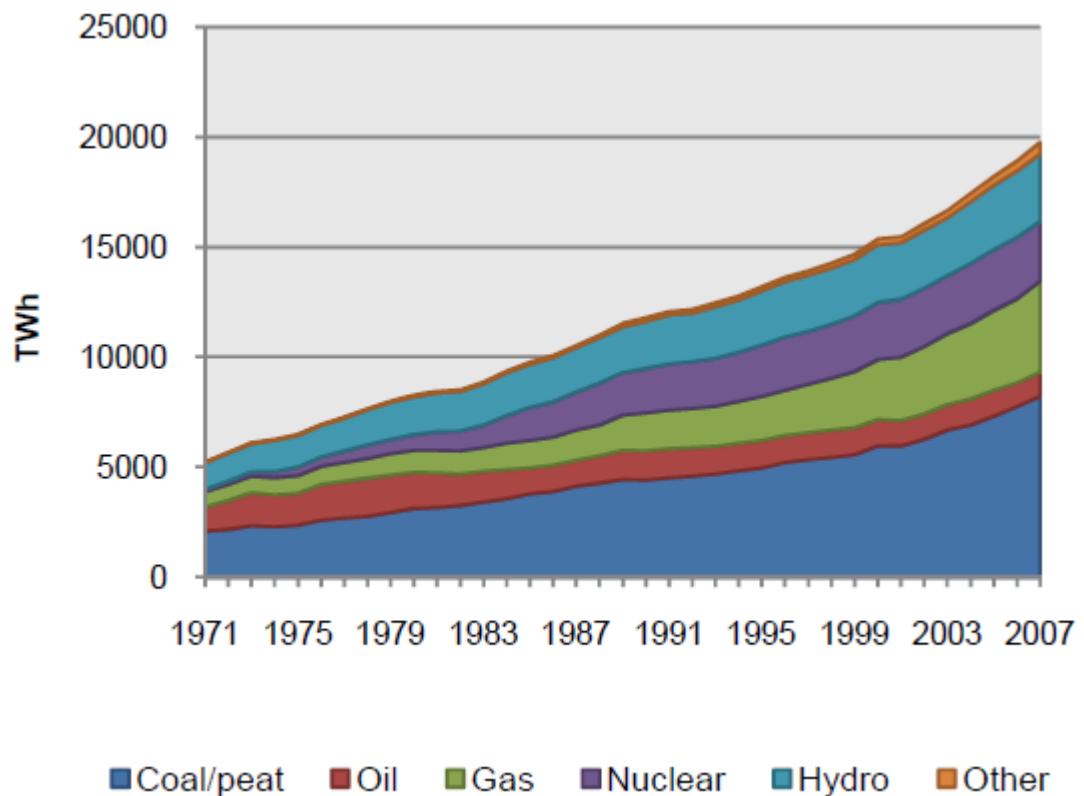
Figure 2. Electricity generation sources between 1971 and 2007 (IEA 2009).

As Figure 2 shows, electricity is nowadays produced four times the amount of that in the beginning of 1970's. Electricity produced with coal, gas and nuclear power has especially risen. Hydropower production has also doubled. About two thirds of the electricity is generated by fossil fuels (coal, oil and gas in the picture). Figure 3 shows the world's CO_2-emissions by different fuels. The Figure shows that CO_2 emissions from fuels have doubled from the 1970's. (IEA 2009)
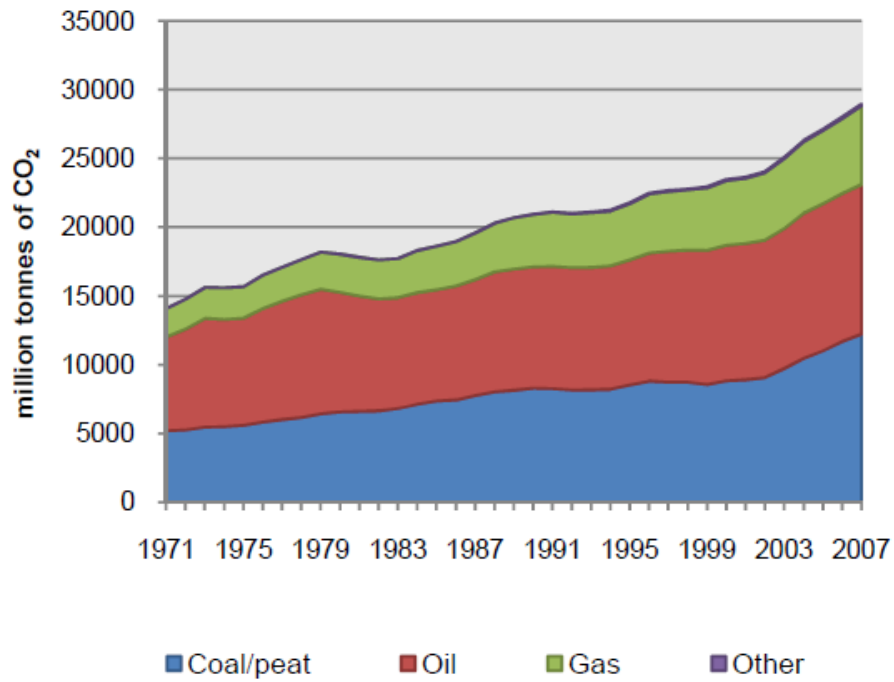
Figure 3. Global CO_2 emissions by fuel in the world (IEA 2009).

Figure 3 shows that oil is as big source of CO_2 as coal. This is mainly because of transportation and heating. Figure 4 shows CO_2-emissions by the sectors using it. (IEA 2009)
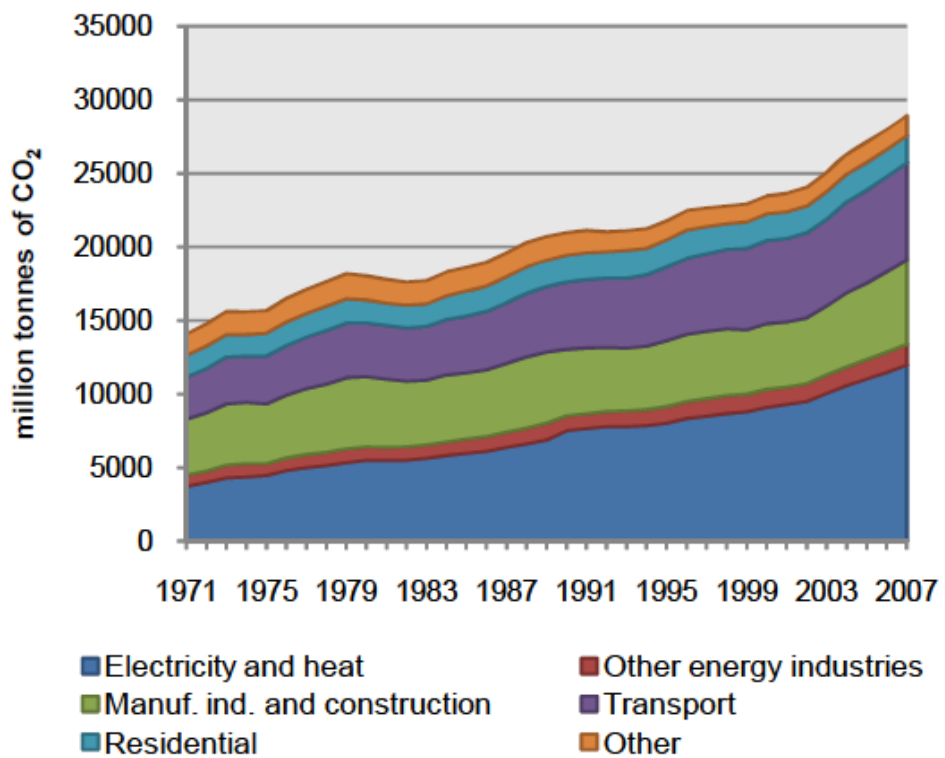
Figure 4. CO_2-emissions by the sector (IEA 2009).

As seen from Figures 3 and 4, fossil fuels are the biggest sources of CO_2. Especially electricity, heating and transportation emit a lot of CO_2, all of which are mostly based on fossil fuels.

There is a growing interest in recovering CO_2 from power station flue gases, but separation techniques are still expensive and are not commonly used on a large scale (Aresta 2006, 1). According to Raudaskoski et al. (2009) CO_2 capture could be applied to all kinds of combustion processes, but the most suitable sources for CO_2 separation are large scale point sources such as power plants and manufacturing industries.

2.3   Thermodynamics of carbon dioxide

CO_2 and H_2O are thermodynamic end products of combustion of materials containing hydrogen and carbon. Carbon dioxide is the most thermodynamically stable of all the carbon-containing binary compounds. However, there are longer carbons containing compounds, such as carbonates that contain the "CO_3" moiety. These are even more stable than CO_2. (Aresta 2006, 5)

The stability of CO_2 has generated the common belief that it is not feasible for reactions and any of its reactions will need so much energy that it will make the use of CO_2 for the syntheses of chemicals demanding. However, there is a number of reactions in which there is no need for any external energy supply. The other reactants involved will bring enough energy for the reaction with CO_2 to occur at room temperature or even below that. For example, the reactions of CO_2 with hydroxide, amines or olefins are like this. (Aresta 2006, 5)

Aresta (2006, 5) has pointed out that the "inertness" of CO_2 can be utilized with oxidants such as O_2. CO_2 behaves as a great combustion regulator or suppressor in these cases. In Table 2 thermodynamic data for many chemicals relevant to CO_2 chemistry is listed (Aresta 2006, 5).

Table 2. Energy of the formation of some chemicals relevant to CO_2 chemistry (Aresta 2006, 5).

Compound	$\Delta H°_r$ (kJ/mol)	$\Delta G°_r$ (kJ/mol)	$\Delta S°_r$ (kJ/ °C)
CO (g)	− 110.53	− 137.2	830.34
CO_2 (g)	− 393.51	− 394.4	897.96
CO_2 (l)		− 386	
CO_2 (aq)	− 413.26		
CO_3^{2-} (aq)	− 675.23		
CaO (s)	− 634.92		
HCO_3^- (aq)	− 689.93	− 603.3	160.02
H_2O (l)	− 285.83		
H_2O (g)	− 241.83		
$CaCO_3$ (s) (calcite)	− 1207.6	− 1129.1	385.14
$CaCO_3$ (s) (aragonite)	− 1207.8	− 1128.2	369.6
$COCl_2$ (g)	− 219.1	− 204.9	1188.6
CS_2 (l)	89	64.6	635.46
CS_2 (g)	116.6	67.1	998.76
HCN (l)	108.9	125.0	473.76
HCN (g)	135.1	124.7	847.56
CH_2O (g)	− 108.6	− 102.5	918.96
HCOOH (l)	− 424.7	− 361.4	541.8
HCOOH (g)	− 378.6		541.8
CH_4 (g)	− 74.4	− 50.3	782.46
CH_3Cl (g)	− 81.9		
H_2NCONH_2 (s)	− 333.6		
CH_3OH (l)	− 239.1	− 166.6	532.56
CH_3OH (g)	− 201.5	− 162.6	1007.16

As Table 2 shows, carbonates have the lowest enthalpy value (CO_3 alone is - 675.23 kJ/mol). The formation of inorganic carbonates from CO_2 and oxides are typically exothermic reactions, but have high kinetic barriers that make their reactions rather slow. The natural weathering of silicates that converts silicates into carbonates (Eq. 1) and free silica is kinetically a slow process that requires activation to occur in solution (Aresta 2006, 5).

$$M_2SiO_4 + 2CO_2 \rightarrow 2MCO_3 + SiO_2 \tag{1}$$

Aresta (2006, 5) classifies generally the reactions of CO_2 into two categories by their energetics:

1. Reactions, which do not require any external energy input, such as those reactions where the carbon atom maintains the +4 oxidation state. These kinds of reactions produce carboxylates and lactones (RCOOR'), carbamates

(RR'NCOOR''), ureas (RR'NCONRR'), isocyanates (RNCO) and carbonates [ROC(O)OR'].

2. Reactions that generate reduced forms of carbon dioxide and require energy. Examples of these are HCOO-(formates), $[C(O)O]^{2-}_2$ (oxalates), H_2CO (formaldehyde), CO, CH_3OH and CH_4.

The energy for the latter reactions can be provided as heat (thermal processes), electrons (electrochemical processes) or irradiation (photochemical processes) Aresta (2006, 5). Sakakura et al. (2007) and Mikkelsen et al. (2009) have introduced another way how to classify the main methodologies how to transform CO_2 into useful chemicals. They used the following four factors:

1. Using high-energy starting materials such as hydrogen, unsaturated compounds, small-membered ring compounds and organometallics.

2. Choosing low energy synthetic targets such as organic carbonates (similar to Aresta's second category)

3. Removing a particular compound from the product side and thus shifting the equilibrium.

4. Supplying physical energy such as light or electricity (similar to Aresta's first category).

The feasibility of developing a process based on CO_2 does not depend necessarily on its exergonicity. Many industrial processes used today are strongly endothermic and therefore consume significant amounts of energy and produce large quantities of waste. Therefore, the feasibility of developing a process based on CO_2 for replacing a conventional process must be analyzed by comparing the two processes. The use of CO_2 will be feasible if it minimizes the material and energy consumption and the CO_2 emissions. (Aresta 2006, 5)

According to Aresta (2006, 5) practically every CO_2 reaction will require a catalyst, which is usually a metal complex. After the first transition metal complex of CO_2 was discovered, the study has been emphasized to the coordination chemistry of CO_2 with the aim being a discovery of new catalysts for the chemical utilization of CO_2.

2.4   Carbon taxes

Today many countries use carbon taxes for lowering the greenhouse gas emissions to the Kyoto protocol. The European Union have agreed to cut the greenhouse gas emissions by 8% from the levels of 1990 within the years 2008-2012. (Ympäristöministeriö 2012)

Finland belongs to the EU Emissions Trading System (EU ETS) that is the cornerstone of EU's policy to fight against climate change and the main tool for reducing industrial greenhouse gas emissions cost-effectively. The 2005 launched EU ETS is the first and biggest international scheme for the trading of greenhouse gas emission allowances. (European Commission 2011)

EU ETS has a cap and trade principle which means that there is a cap or limit on the total greenhouse gas amount that a factory, power plant or other installation can emit. Within this cap corporations receive emission allowances that they can sell or buy from another company or party player when needed. (European Commission 2011)

Finland was the first nation to adopt a carbon tax in 1990. Carbon tax in Finland is used for transportation and heating. The carbon tax applies to gasoline, diesel, light and heavy fuel oils, jet fuel, aviation gasoline, coal, and natural gas. Coal is subjected to a tax of about 50 € per metric ton, natural gas of about 2 € per MWh, and liquid fuels are taxed between 0.05 and 0.06 € per litre. Commercial vessels and commercial air traffic as well as fuels used for electricity are exempt. Electricity has set a tax but the rate per kWh is not dependent on the carbon content. However, renewable electricity may receive a refund. Finland's carbon tax revenues are budgeted annually at 500 million €. During the latest years this has meant a CO_2 tax of about 10 € for metric ton of CO_2. (Sumner et al. 2009)

3   Capture and separation of carbon dioxide

There are three technologies that can be used for capturing carbon dioxide from coal-derived power generation: post combustion capture, pre-combustion capture, and oxy-combustion. The block diagrams of these diagrams are represented in Figure 5. (Figueroa et al. 2008)
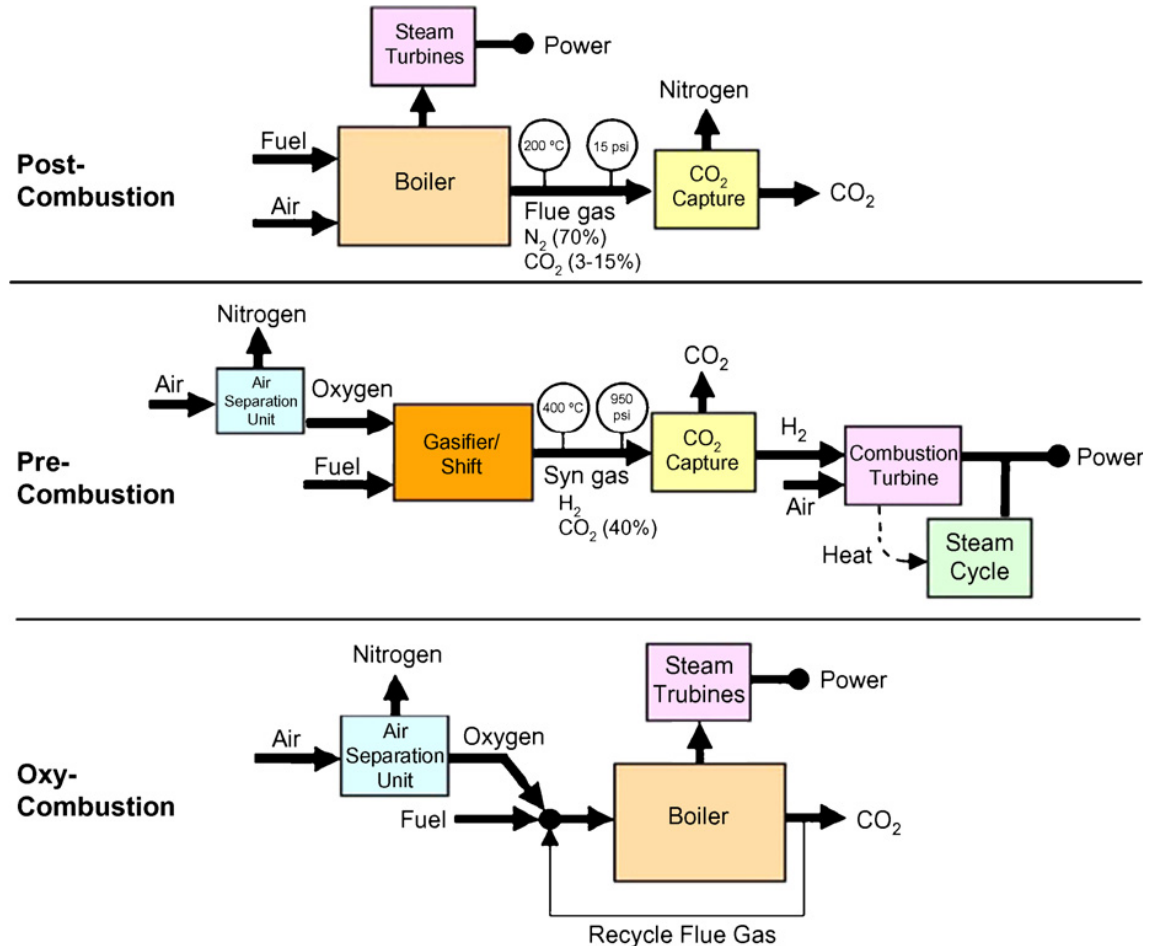
Figure 5. Block diagrams illustrating post-combustion, pre-combustion and oxy-combustion systems (Figueroa et al. 2008).

As shown in Figure 5, in the post-combustion capture carbon dioxide is separated from the other flue gas components either originally present in the air or produced by combustion. In the pre-combustion capture carbon dioxide is separated from the generated synthesis g
as fuel stream before combustion and in the oxy-combustion the fuel is burned in a pure oxygen stream. (Figueroa et al. 2008)

3.1 Post-combustion capture

Figueroa et al. (2008) have claimed that the typical flue gas mixture has 3-15 mol-% CO_2. However as high as 20 mol-% exists according to e.g. Adeyemo et al. (2010). It is obvious that the capturing would be more effective if done in a plant producing flue gas containing 20 mol-% CO_2.

Figueroa et al. (2008) have stated that the thermodynamic driving force for CO_2 capture is low with the CO_2 partial pressure being typically less than 0.15 atm. This fact provides a great challenge and big difficulties for the researchers working on a cost effective capture process. Despite the difficulties, the post-combustion capture has the biggest short-term potential for the reduction of GHGs. Basically this is due the fact that it can be placed to existing units that create two-thirds of the CO_2 emissions in energy production. The post-combustion capture can be done with absorption, adsorption or membranes. (Yang et al. 2008)

3.1.1 Absorption

The most studied CO_2 absorption systems are the amine based systems. Monoethanolamine (MEA) is used in natural gas industry to absorb CO_2 from natural gas. Diethanolamine (DEA) and methyldiethanolamine (MDEA) are also often used. Figure 6 shows the reaction sequence for the capture of CO_2 with liquid amine-based systems. (Yang et al. 2008)

Figure 6. Reaction mechanism of CO_2 capture by amine-based systems (Yang et al. 2008).

As seen from Figure 6, amines react with CO_2 producing carbamates and carbonates. These products are water soluble compounds. Because of the formation of new compounds, amines can capture CO_2 from streams with even a rather low

CO_2 partial pressure but the capacity is limited by the reaction equilibrium. Amine-based systems work well in recovering CO_2 from the flue gas of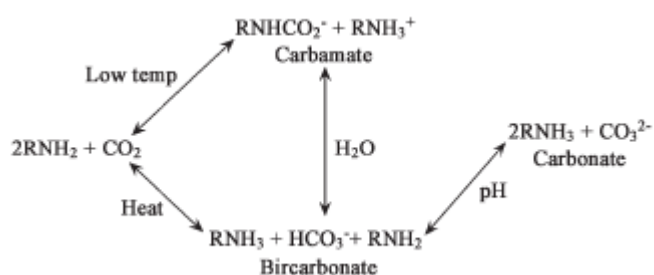 conventional pulverized coal fired power plants but the equilibrium makes them rather costly and non-efficient. Process improvements are needed especially in the removal of acid gases from natural gas in spite of the fact that amines have been used for many years commercially. (Figueroa et al. 2008)

Amines can be obtained in three forms (primary, secondary and tertiary). Improved amine-based systems are also being researched. Reduced pressure drop, capacity increase and better heat integration have all been reported. Additives within the amine solvent can reduce corrosion and allow higher amine concentrations thus improving amine regeneration. (Figueroa et al. 2008, Yang et al. 2008)

An alternative absorption system is the ammonia-based wet scrubbing. In this process the flue gas is pre-treated by oxidizing SO_2 and NO to SO_3 and NO_2, respectively. After that the flue gas reacts with aqueous ammonia in a wet scrubber producing ammonium carbonate and ammonium bicarbonate. Ammonium sulphate and ammonium nitrate can also be formed with SO_x and NO_x which are present in the flue gas. Ammonium sulphate and nitrate can be used as fertilizers but ammonium bicarbonate does not have so far any relevant utilization. (Figueroa et al. 2008, Yang et al. 2008)

Carbonate formation has significantly lower heat of reaction than the reactions taking place in amine-based systems. This lowers energy costs. Other advantages over the amine-based systems include potential for higher CO_2 capacity, lack of degradation during absorption and regeneration, tolerance of O_2 in flue gas, overall lower costs and potential for regeneration at high pressure. Downsides are that the flue gas needs to be cooled to enhance the CO_2 absorptivity of ammonia compounds and to minimize gaseous ammonia emissions during the absorption stage. Ammonia losses during regeneration are also a concern. Improvement of the process concentrates on the vapour losses from the system during operation and higher CO_2 loading via process optimization. (Figueroa et al. 2008, Yang et al. 2008)

Carbonate systems base also on lower energy consumption required for regeneration. In the carbonate systems CO_2 reacts with carbonate forming bicarbonate which is then heated to release CO_2 and carbonate. One example reaction is the sodium carbonate (Na_2CO_3) that reacts with CO_2 and water forming $NaHCO_3$. (Yang et al. 2008)

3.1.2 Adsorption

Many solids can be used to adsorb CO_2. No water has to be used in adsorption which is an advantage. Sorbents can be treated with amines or other chemicals to react with CO_2 forming stable compounds. No large scale recovery of CO_2 via adsorption exists although sorbent systems are used commercially for example in the production of pure H_2. Various amine compounds can be used as sorbents. Also carbonates can be used. In the case with carbonates the formed bicarbonate is regenerated with a temperature swing to produce a pure CO_2/water stream. Research concentrates on problems associated with pressure drop and heat transfer of solid sorbents. An example of one amine-enriched sorbent (MCM-41) process and its properties are presented in Figure 7. This molecular sieve shown in Figure 7 has been impregnated into the structure to act as the active site. (Figueroa et al. 2008, Yang et al. 2008)

$$\left(-NHCH_2CH_2\right)_{x}\left(-\underset{\underset{CH_2CH_2NH_2}{|}}{N}-CH_2CH_2-\right)_{y}$$

MCM-41   Polyethylenimine

- Uniform, "tailorable" 15-100 A mesopores
- Narrow pore size distribution
- High surgace area
- Large pore volume
- High thermal stability
- High amine group density, large amount of CO_2 adsorption sites

- Secondary and tertiary amine facilitate desorption
- Viscous liquid
- Slow CO_2 adsorption/desorpt kinetic

Figure 7. Structures and properties of MCM-41 and polyethylenimine (Yang et al. 2008).

3.1.3 Membranes

There are a lot of options for the post-combustion membrane separation. Flue gas can be passed through a bundle of membrane tubes with an amine solution flowing though the shell side and reacting with CO_2. Amine is regenerated and recycled after the reactions. Amine functional groups can be used also with microporous inorganic silica membranes. Zeolites, crystalline aluminosilicate materials, with high surface area are also studied. Figure 8 shows the schematic of an amine solvent using a gas absorption membrane. (Figueroa et al. 2008, Yang et al. 2008, Ciferno et al. 2009)
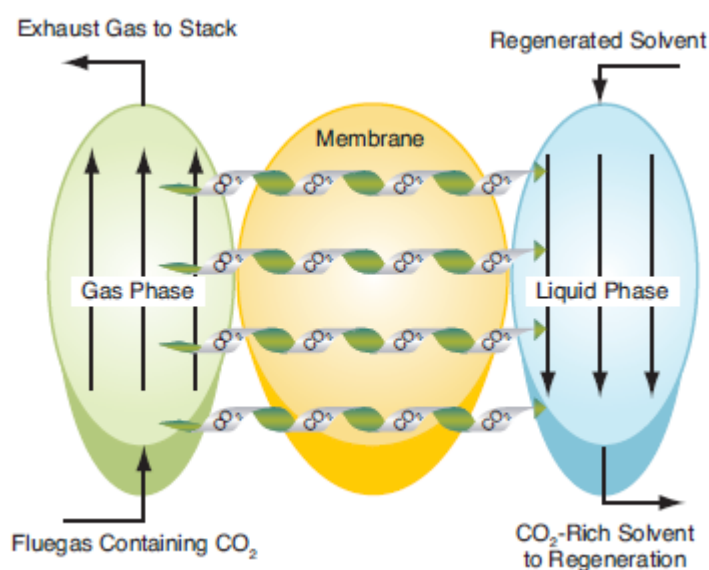
Figure 8. Schematic of a solvent using gas absorption membrane (Ciferno et al. 2009).

3.2 Pre-combustion capture

Pre-combustion capture is basically a separation of carbon dioxide from a CO_2-CO-H_2-mixture. One promising approach to the pre-combustion capture is the integrated gasification combine cycle (IGCC). In this method coal is gasified with oxygen to produce syngas. Syngas added with steam is sent to a shift converter where water gas shift reaction ($CO + H_2O \rightarrow CO_2 + H_2O$) converts CO to CO_2 and additional H_2. CO_2 is separated and H_2 mixed with steam or nitrogen is sent to a combustion turbine. In factories, the fuel gas is mostly H_2 (about 60 mol-%) and CO_2 (about 40 mol-%) coming out from the IGCC. The pressure used is between 2.5–7 MPa. The fuel gas mixture is pre-treated for the removal of particulate matter and H_2S. Other

pre-combustion methods include physical solvent processes, membranes, sorbents or improved auxiliary processes. (Figueroa et al. 2008, Adeyemo et al. 2010)

Pre-combustion capture has the advantage of high concentrated and high pressurized synthesis gas which results in high CO_2 partial pressures. Increased CO_2 partial pressure increases the driving force for separation and makes the separation process easier. High pressure of the syngas might lower the compression costs/loads in further stages of the process. (Figueroa et al. 2008)

3.3 Oxy-fuel combustion

In oxy-combustion the combustion process is modified so that the flue gas has a high concentration of CO_2. Fuel is burned with nearly pure oxygen (95 %) mixed with recycled flue gas. A cryogenic air separation unit is used to supply high purity oxygen to the boiler. Oxy-combustion creates a very high CO_2 concentration in flue gas which makes the separation less energy consuming. It creates also possibilities for retrofitting and repowering technologies. Barriers for implementation include the large cryogenic O_2 production requirement which might make the process cost prohibitive. The cooled CO_2 recycle required to maintain temperatures within limits of combustor materials decreases also the process efficiency and adds auxiliary loads. (Figueroa et al. 2008)

3.4 Chemical looping combustion

One method of the pre-combustion capture is the chemical looping combustion (CLC) where oxygen is supplied by a solid oxygen carrier rather than by air or gaseous oxygen. CLC has several advantages compared to conventional combustion. The exhaust gas stream from an air reactor is harmless, consisting mainly of N_2. In a well-designed system, there should be no thermal formation of NO_x since the regeneration of oxygen carrier takes place without a flame and at moderate temperatures. The exhaust gas from the fuel reactor consists of CO_2 and H_2O. Separation of CO_2 can be done by a condenser. This is the major advantage with CLC which avoids the huge energy penalty necessary in traditional amine scrubbing process to capture CO_2. (Yang et al. 2008)

3.5   Energy requirements and costs of carbon capture

Table 3 shows the energy requirements for different CO_2 capture processes.

Table 3. Energy required for removing and recovering CO_2 from a coal-fired power plant (Halmann & Steinberg 1999, 137).

Capture process	CO_2 removal efficiency	kWh/kg CO_2 removed
Improved amine absorption/stripping integrated plant	90	0.243
Oxygen/coal-fired power plant	100	0.331
Amine (MEA) absorption/stripping nonintegrated plant	90	0.596
Potassium sieves adsorption/stripping	90	0.706
Molecular sieves adsorption/stripping	90	0.883
Refrigeration	90	0.888
Seawater adsorption	90	1.766
Pressurized fluidized bed combustor seawater pressure equalized	99	0.397
Membrane separation	90	0.795

As Table 3 summarizes, there are big differences among the energy consumptions in different capture methods. Another study of the energy consumptions of different capture methods was conducted by David and Herzog (2000) who researched the cost of CO_2 separation and capture in three types of power plants, integrated coal gasification combined cycles (IGCC), pulverized coal-fired simple cycles and natural gas-fired combined cycles (NGCC). In their study MEA scrubbing was used as the capture method for the pulverized coal-fired simple cycle and NGCC plants. For IGCC the used capture process was physical absorption to give a more energy efficient scrubbing process from the high pressure synthesis gas. The results of the research year (2000) and predictions for 2012 of the study are listed in Table 4.

Table 4. Energy required for removing and recovering CO_2 in different types of power plants (David and Herzog, 2000).

Case plant	CO_2 capture method	kWh/kg CO_2 removed
IGCC (2000)	Physical absorption	0.194
IGCC (2012)	Physical absorption	0.135
Pulverized coal-fired simple cycle (2000)	Chemical absorption (MEA)	0.317
Pulverized coal-fired simple cycle (2012)	Chemical absorption (MEA)	0.196
NGCC (2000)	Chemical absorption (MEA)	0.354
NGCC (2012)	Chemical absorption (MEA)	0.297

As Tables 3 and 4 show, there are differences in the energy consumptions of different capture processes between studies. Also Berstad et al. (2011) calculated the specific capture and compression work for cases of NGCC, coal and biomass power plants (Figure 9). Figure 9 depicts the reversible specific capture and compression power for 90% capture as a function of dry flue-gas fraction of CO_2.
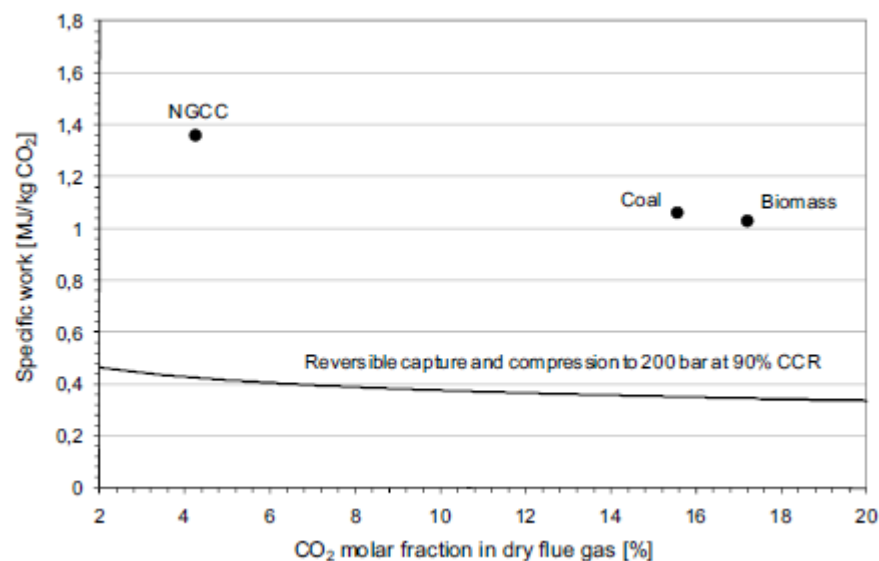
Figure 9. Specific capture and compression work for cases of NGCC, coal and biomass power plants with CO_2 capture with a plot of reversible specific capture and compression power for 90% capture as a function of dry flue-gas fraction of CO_2 (Berstad et al. 2011).

As Figure 9 shows, in the flue gas in the case of NGCC the same amount of energy per CO_2 ton was captured but it manages to do this from a small molar fraction of CO_2. Rubin et al. (2007) reported the current post-combustion separation costs from a pulverized coal power plant being at 30-50 €/ton of CO_2. Davison (2007)

claimed the capture costs being at 16-32 € / ton of CO_2 for Shell GE and Selexol's IGCC-CCS process. Noteworthy is that these prices include only the capture.

McKinsey (2011) has calculated also the other costs of the whole CCS chain. The calculated capture costs were at 25–32 €/ton of CO_2. Transport was estimated to be 4–6 €/ton and storage 4–12 €/ton. Later in this thesis the used values for CO_2 separation are 10, 20 and 30 €/ton (10 €/ton being a clear future estimate) which are rather close to the costs calculated by McKinsey (2011) (Teir et al. 2011).

4   Industrial applications of carbon dioxide

CO_2 is utilized as an important source of carbon for synthesizing organic chemicals, materials and even foods. Various chemicals, materials and fuels can be produced using carbon dioxide which provides a sustainable way to mitigate GHG emissions while producing new synthetic products to replace virgin natural resources. (Song 2006)

4.1   Carbon dioxide use in industry and potential market growth

CO_2 is already used in industrial processes as an ingredient. Still, the industrial use (120 Mt) amounts to only 0.5% of the total anthropogenic carbon dioxide emissions (about 24 Gt every year). Aresta (2007) and Mikkelsen et al. (2010) gathered information about the CO_2 use and potential market growth for different chemical applications (Table 5).

Table 5. Annual industrial volume of a product or application, industrial use of CO_2, future expectation in the use of CO_2 and the lifetime of a product (Aresta 2007 & Mikkelsen et al. 2010).

Product or application	Market (Mt)	Amount of CO_2 used (Mt)	Future expectation (CO_2 used)	Lifetime of product
Urea	98–100	70–72	10^2 Mt	6 months
Methanol	35–40	7–14	Gt	6 months
Inorganic carbonates	80	30		Decades
Organic carbonates	2.6	0.2	10^2 Mt	Decades to centuries
Salicylic acid	0.06	0.06	10^2 kt	
Technological	10–11	10–11		Months to years
Food	8	8		Months to years

A shown in Table 5, the biggest user of CO_2 is the fertilizer industry with the CO_2 utilizing reaction of urea synthesis as the main reaction. Inorganic carbonates use also a rather big amount of CO_2. CO_2 use in methanol production is also rising all the time. Mikkelsen et al. (2010) have pointed out high future expectations for methanol use apparently mostly as a fuel.

4.2 Direct utilization of CO_2

Carbon dioxide usage can roughly be divided into two categories: direct use of CO_2 which uses its physical preferences and chemical use of CO_2 that uses its chemical properties. The physical aspects are used for example in beverage industry and in enhanced oil recovery. Direct use of CO_2 includes also supercritical CO_2 use as a technological fluid in nano-particle or composite production and as a solvent. CO_2 as an inert and safe gas is also used as a protective gas and as a fire extinguisher. Solid state CO_2 is used as refrigerant in railcars and trailers to substitute the use of CFCs, which have been shown to be harmful to the atmosphere already in small concentrations. Table 6 shows existing direct carbon dioxide applications by Turunen (2011). (Mikkelsen et al. 2010)

Table 6. Direct usage applications of CO_2 (Turunen 2011).

Purpose of CO_2	Objective
Solvent under the supercritical or liquid state	Extraction processes of coffee, tea, hops, plants, berries and other similar applications in food processing industry Spray coating and particle formation
Cleaning medium	Dry cleaning, under the supercritical state Dry ice blasting with frozen CO_2
Shielding gas	Food packing Welding Fire extinguishers (fixed and portable)
Cooling medium	Refrigerating systems Direct cooling with dry ice
Product formulator / additive	Brewery and soft drink industry
pH agent	Pulp and paper industry and water treatment (replaces sulphur treatment) Neutralisation (swimming pool, water treatment)
Filling gas	Enhanced oil recovery (EOR)

4.3 Chemical utilization of CO_2

4.3.1 Urea

The commercial production of urea has the biggest share of the chemical utilization of CO_2 (about to 70 million tonnes of CO_2 used per year). The production process occurs at elevated pressure (150 to 250 bars) and temperature (150 to 200 °C). The first step is the reaction of ammonia and CO_2 to form ammonium carbamate. In the

second step the dehydration of the carbamate to urea is conducted. The stages of the process are depicted in Figure 10. (Mikkelsen et al. 2010)

$$2NH_3 + CO_2 \rightleftharpoons H_2NCO^{\ominus} NH_4^{\oplus} \xrightarrow{-H_2O} H_2NCNH_2$$
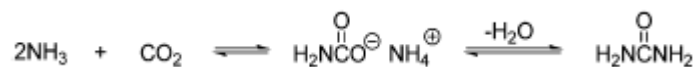
Figure 10. Industrial production of urea from CO_2 and ammonia (Mikkelsen et al. 2010).

Urea is produced with different techniques concerning the recovery and recycling of the unreacted ammonium carbamate but the basic two reaction steps (Figure 10) are always the same. Urea is used as a chemical fertilizer, urea resins, urea-melamine resins and as an animal feed additive. (Mikkelsen et al. 2010)

4.3.2 Inorganic carbonates

Inorganic carbonates have the second biggest share of the world's chemical utilization of CO_2 (use of 30 million Mt per year). These processes include for example the carbonation reactions with CaO (Eq. 2) and MgO (Eq. 3) (Lackner et al. 1995):

$$CaO + CO_2 \rightleftharpoons CaCO_3 \tag{2}$$
$$\Delta H_{298\ K} = 179\ kJ/mol$$

$$MgO + CO_2 \rightleftharpoons MgCO_3 \tag{3}$$
$$\Delta H_{298\ K} = 118\ kJ/mol$$

Basic absorbents such as calcium hydroxide ($Ca(OH)_2$) or potassium hydroxide (KOH) are used to react with CO_2 and form carbonates. For example synthetic precipitated calcium carbonate (PCC) production uses this method. CaO is produced from limestone (major components calcium carbonate and magnesium calcium carbonate). Limestone is calcinated to form CaO which is then treated with water to form $Ca(OH)_2$. $Ca(OH)_2$ is carbonated using CO_2. (Mikkelsen et al. 2010)

Besides CaCO$_2$, CO$_2$ is used also in preparation of NaHCO$_3$ and Na$_2$CO$_3$ and many other carbonates (Table 7). Many of these are formed by reaction with an aqueous solution of the corresponding oxide and supercritical CO$_2$. The reaction temperatures in these processes are low (25–45 °C), pressures are high (70–250 bar) with yields above 95 % of the desired product. (Mikkelsen et al. 2010)

Table 7. Market volumes with the amount of CO$_2$ used for different inorganic carbonates (Mikkelsen et al. 2010).

Product	Market (Mt/year)	CO$_2$ used (Mt/year)
Na-carbonate	35	Less than 15
Na-bicarbonate	5	
Ca-carbonate	Several thousand	Mainly mined
Ca-carbonate PCC	Less than 7	Less than 3.5
K-carbonate	0.1-0.2	0.03-0.05
K-bicarbonate	Less than 0.01	Less than 0.01
Mg-carbonate	3.5	Mainly mined
Ba-carbonate	0.02-0.03	Less than 0.01
Li-carbonate	0.01-0.02	Less than 0.01
Sr-carbonate	0.3-0.4	Less than 0.1

As Table 7 shows, Na- and Ca-carbonate production use a lot of CO$_2$ compared to the other carbonate groups.

4.3.3 Methanol

Methanol synthesis uses the third biggest amount of CO$_2$ as a starting compound. Industrially, methanol is produced via the synthesis gas route. (Fiedler et al. 2012) The methanol synthesis from syngas is expressed with the formula (4). (Kroschwitz 1995)

$$CO + 2H_2 \rightleftharpoons CH_3OH \tag{4}$$

Other two reactions that have been shown to take place in methanol synthesis are the CO$_2$ utilizing reaction (5) and the water gas shift (WGS) reaction (6) (Kroschwitz 1995).

$$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O \tag{5}$$
$$CO + H_2O \rightleftharpoons CO_2 + H_2 \tag{6}$$

The methanol producing reaction (5) is exothermic and reduces volume. The conversion thus gets better at low temperatures and high pressures. (Tijm et al. 2001) The syngas is from natural gas or coal source the main ingredients being CO and H_2 with a small amount of CO_2. The reaction is driven with copper/zinc oxide based catalysts which provide a high reactivity and selectivity for the process. Equation 7 shows an example of the mole balance of the feed flow in industrial methanol synthesis processes (Mikkelsen et al. 2010).

$$3CO + 9H_2 + CO_2 \rightleftharpoons 4CH_3OH + H_2O \tag{7}$$

As Equation 7 shows, the reaction requires much more syngas moles compared to CO_2 moles. Because of the large amount of syngas needed, methanol plants are usually placed near syngas plants (KBR 2011).

4.3.4 Organic carbonates

Carbon dioxide can react with epoxides to give cyclic carbonates as a product. The process is driven in the presence of quaternary ammonium halides. The synthesis of five membered cyclic carbonates (ethylene and propylene carbonate) has been industrialized since 1950s. The synthesis is shown in Figure 11. (Mikkelsen et al. 2010)
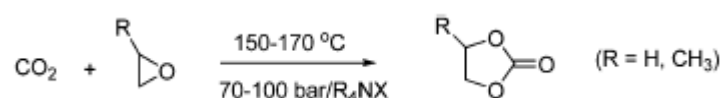
Figure 11. Synthesis of cyclic carbonates from CO_2 and epoxides (Mikkelsen et al. 2010).

As Figure 11 shows, temperature used is rather low but high pressures are needed in the process. Cyclic carbonates can be used as solvents due to their high boiling point. They can also react with ammonia or amines to form carbamates. Carbamates are important as they can be converted into polyurethane – a material with a high commercial value. Alkene carbonates generally are very good solvents for the

production of many polymers as e.g. polyacrylonitrile, nylon, terylene and polyvinylchloride. (Mikkelsen et al. 2010)

Another industrial CO_2 utilizing process, the polycarbonate production process comprises the same reactants as in the synthesis of five-membered cyclic carbonates shown in Figure 11 (Mikkelsen et al. 2010). This process was introduced by Asahi Kasei Corporation (Fukuoka et al. 2003).

4.3.5 Carboxylic acids

Phenolic potassium or sodium salts are converted into carboxylic acids by reaction with carbon dioxide. The annual use of CO_2 in these processes is very small compared to the other users. In pharmaceutical industries, the preparation of numerous products and dyestuff intermediates, e.g. o- and p-hydrobenzoic acids, p-aminosalicylic acid, 2-hydroxynaphthalene-3(and6-)-carboxylic acids and 2-hydroxycarbazole-3-carboxylic acid have been produced. (Mikkelsen et al. 2010)

A traditional example of important acids prepared by the Kolbe-Schmitt process is salicylic acid, which is an intermediate in the production of acetylsalicyclic acid (Aspirin). This reaction (Figure 12) has been used in the industrial production of salicyclic acid since 1874. In the industrial process CO_2 is introduced under 5–7 bar pressure to provide a yield increase from 50% to 90%. The process is driven by heating sodium salt under pressure in an autoclave. The salicylic acid is recovered by acidification with H_2SO_4. (Mikkelsen et al. 2010)
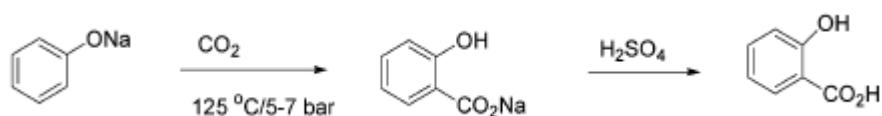
Figure 12. Industrial synthesis of salicylic acid (Mikkelsen et. al. 2010).

5   Reforming (synthesis gas production)

Reforming is a method to produce useful products from fossil fuels. Reforming is used to produce hydrogen or hydrogen-carbon oxide mixtures; the basis of many basic chemicals such as ammonia, methanol and many oil refining products. The compared processes are the conventional steam methane reforming process and the CO_2 utilizing dry reforming process. (Häussinger et al. 2012)

5.1   Steam methane reforming

5.1.1 Overview of the process

Methane steam reforming (SMR) was invented by BASF in 1920s. The catalytic endothermic process for gaseous hydrocarbon conversion to gas was produced in externally heated tubes with nickel as a catalyst. The first commercial applications produced hydrogen for hydrogenation and ammonia synthesis at atmospheric pressure. Nowadays new reformer tube materials allow higher pressures to improve plant efficiency. In steam methane reforming hydrocarbons are converted to CO and H_2 as shown in Equation (8) (Häussinger et al. 2012):

$$C_nH_m + n\ H_2O \rightleftharpoons n\ CO + (m/2+n)\ H_2 \qquad (8)$$

Reactions that take place in the system are listed in the following Equations (Liu et al.):

$$CH_4 + H_2O \rightleftharpoons CO + 3\ H_2\ (\Delta H_{298\ K} = +206\ kJ/mol) \qquad (9)$$
$$CO + H_2O \rightleftharpoons CO_2 + H_2\ (\Delta H_{298\ K} = -41\ kJ/mol) \qquad (6)$$
$$2CO \rightleftharpoons CO_2 + C\ (\Delta H_{298\ K} = -172.4\ kJ/mol) \qquad (10)$$
$$CH_4 \rightleftharpoons C + 2H_2\ (\Delta H_{298\ K} = +74.6\ kJ/mol) \qquad (11)$$
$$C + H_2O \rightleftharpoons CO + H_2\ (\Delta H_{298\ K} = +131.3\ kJ/mol) \qquad (12)$$
$$CO + 0.5\ O_2 \rightleftharpoons CO_2\ (\Delta H_{298\ K} = -283\ kJ/mol) \qquad (13)$$
$$CO + 3H_2 \rightleftharpoons CH_4 + H_2O\ (\Delta H_{298\ K} = -205.9\ kJ/mol) \qquad (14)$$
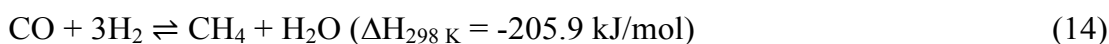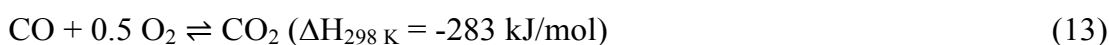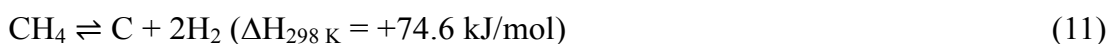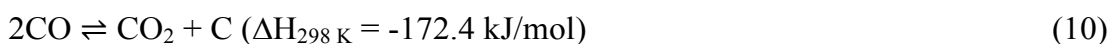
The flowsheet of the steam methane reforming process is shown in Figure 13.
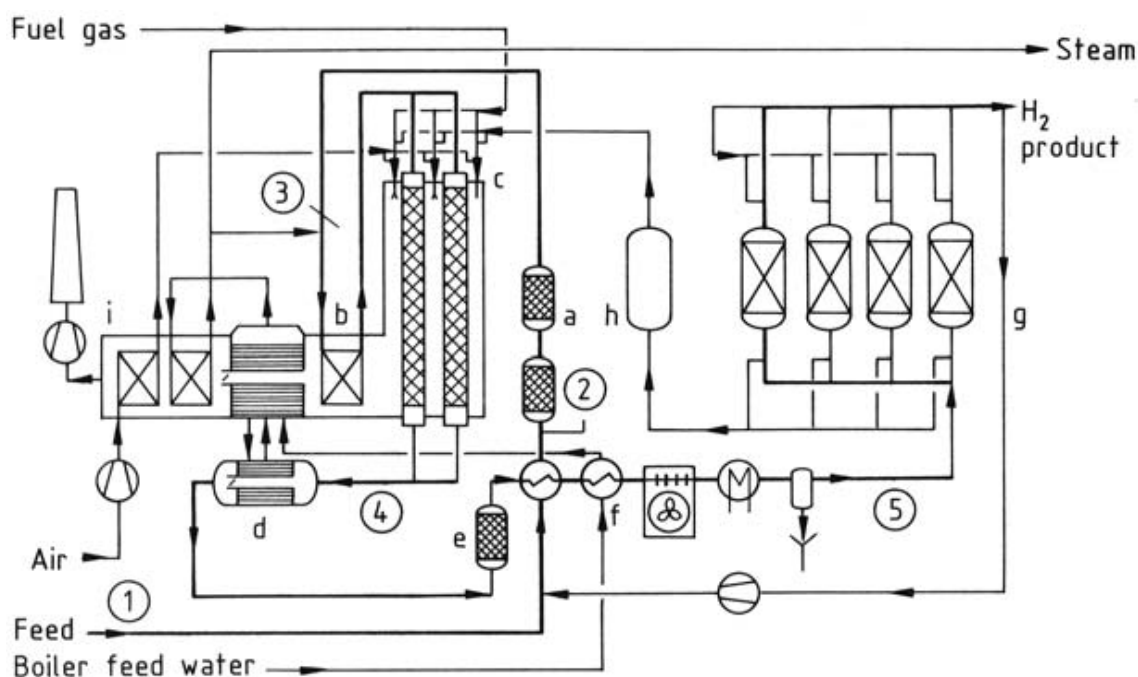
Figure 13. Steam methane reforming process flow sheet (Design: German Linde) a) Desulfurization, b) Feed preheater/superheater, c) Reformer, d) Waste-heat boiler, e) CO shift reactor (HT shift), f) Cooling of raw gas, g) Pressure swing adsorption (PSA) h) Off-gas puffer for fuel, i) Convection zone with steam production, steam superheating and air preheating (Häussinger et al. 2012).

In Figure 13 in desulphurization (13a), small amounts of sulphur compounds existing in natural gas are removed. A zinc oxide bed is used to remove hydrogen sulphide and other sulphur compounds. Possible higher organic sulphur compounds such as mercaptans and thiophene or carbonyl sulphide can be separated by having a hydrogenation stage and desulfurization stage in series. Hydrogenation and desulphurization are done at 350 - 400 °C. Gas leaves the purification section at the same temperature. (Häussinger et al. 2012)

After the preheating/superheating stage (13b) the gas is at temperature of 520 °C. Steam is added to the inlet feed to make the ratio of at least 2.5 moles of steam per carbon mole. In the reformer tube (13c) the reforming reaction takes place over a nickel catalyst the outlet temperature being at 850 °C. Gas is cooled quickly by producing steam in the process gas boiler (13d). According to Vesely et al. (1969) catalyst regeneration is done in an attached regenerator reactor that also dries the catalysts before feeding them back to the reforming reactor. In the reforming

reactor, higher hydrocarbons are completely reformed to CO and H_2 as Eq. (8) shows. (Häussinger et al. 2012)

High-Temperature Shift Conversion (Figure 13e) cools the gas down to 350 °C. The process gas boiler contains still a lot of CO which can be converted into hydrogen with the water gas shift reaction (6). This reaction is catalysed with an iron-oxide based catalyst. The reaction takes place usually in a one-stage adiabatic reactor. Reaction is exothermic which means that the process gas temperature rises to 400–450 °C and the conversion is incomplete. After the shift conversion the gas is cooled down to ambient temperature in the pressure-swing adsorption process (PSA) (13g). Water condensates and is removed before the gas is fed to at least three parallel adsorbers that run in cyclic operation. PSA alternative after the HT shift is the "classical process". In that case the gas is cooled to 220 °C and fed into a low-temperature shift reactor. Carbon dioxide scrubber follows this stage. Catalytic methanation step removes the remaining carbon dioxide and carbon monoxide. Hydrogen purity of 97–99% is achieved with this process. Pure hydrogen plants usually use PSA but the classical route is used if the maximum 99% purity is enough. Table 8 shows the mass balance of a typical steam reformer plant producing 5000 m^3/h hydrogen. (Häussinger et al. 2012)

Table 8. Mass balance of a 5000 m^3/h hydrogen producing facility (Häussinger et al. 2012).

	Feed	Before desulfurization	Reformer inlet	Reformer outlet	PSA	Pure H_2
H_2, vol-%	0	4.8	1.1	51.9	74.6	99.99
N_2, vol-%	1	1	0.3	0.2	0.25	0.01
CO, vol-%	0	0	0	10.7	5.3	0
CO_2, vol-%	0.5	0.5	0.1	5.1	14.8	0
CH_4, vol-%	95	90.4	26.1	3.8	4.9	0
C_{2+}, vol-%	3.5	3.3	1.0	0	0	0
H_2O, vol-%	0	0	71.4	28.3	0.15	0
Quantity, m^3/h	2160	2070	7160	10450	8180	5000.5
T, °C	20	390	520	850	20	20
Pressure, MPa	2.0	1.9	1.9	1.7	1.6	1.5

As Table 8 shows, the reformer outlet does not consist of very pure H_2. The concentration of raw materials is small in the reformer outlet stream. The feed

column shows the typical concentration of the feedstock – natural gas. (Häussinger et al. 2012)

5.1.2 Reactors

The aim of the reactor is to use minimum amount of fuel to obtain maximum temperature at the exit of the reformer tube. Fuel use is minimized if heat is delivered to each reformer tube section corresponding to the heat requirements of the reaction in the tube. The composition of the reformed gas depends on specified conditions (pressure, reformed gas temperature, steam-hydrocarbon ratio). Although the stoichiometry of the reaction (9) suggests that the H_2O/C ratio of 1 should be used in real life processes, in reality the ratio used is 2.5-5 to make sure that no formation of carbon takes place. If CO is the desired product, the S/C ratio is lower. The tubular steam reformer has not changed much during the past 20 years. Particularly new reformer tube materials, heat exchangers and insulation along with better heat management have led to improved and excellent efficiency and reliability. The type of a reformer depends on the plant size. Figure 14 depicts types of reformers depending on the plant size. (Häussinger et al. 2012, Reimert et al. 2012)
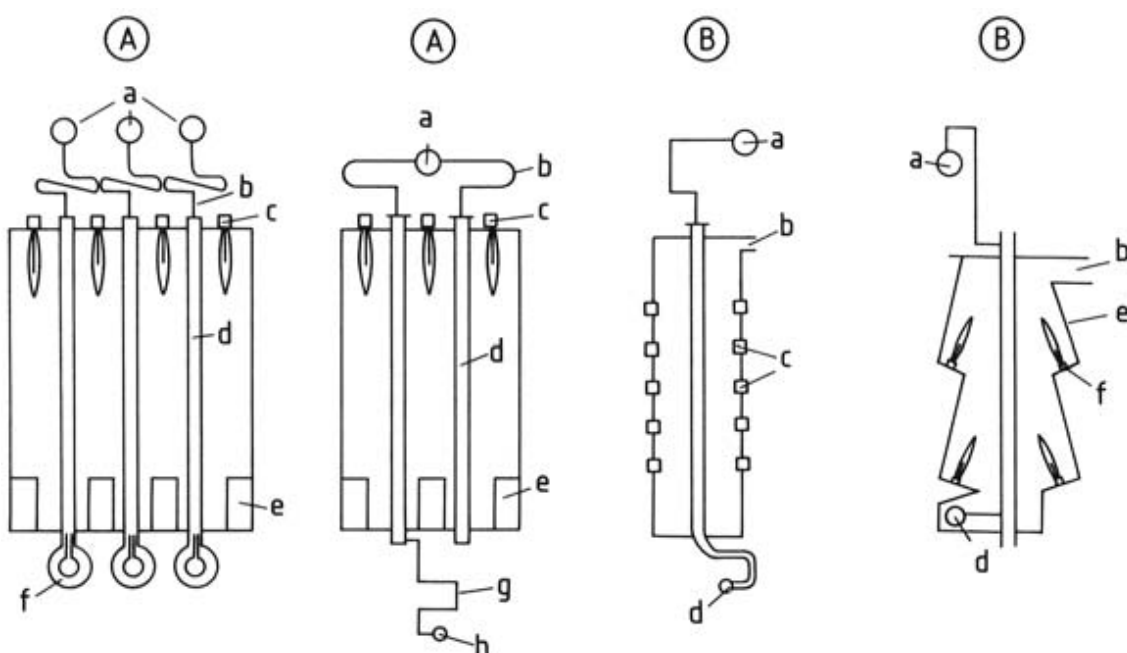
Figure 14. Reformer types, A) Top-fired furnaces, B) Sidewall-fired furnaces (Reiter 2012).

Larger hydrogen plants use the box furnace configuration. The advantage of the box furnace is that it allows an even heat load distribution for each tube. Heat flux can thus be increased. There are various types of box furnaces. The most common is the top-fired furnace (14A) but also bottom-fired, sidewall-fired (14B) and combined types are used. In the top-fired furnace the process gas flows though the tubes from the top to the bottom. Hot outlet gas is typically gathered in a manifold system and let to the process gas boiler. (Häussinger et al. 2012)

5.1.3 New developments in reactor technology

One research area within reactors is the pressurization of the fireboxes. In conventional reformers the pressure is atmospheric or slightly above because it is thermodynamically favourable. However, with higher pressure fireboxes a higher heat transfer from the flue gas to the reformer is achieved. This can be done also with a similar heat exchanger concept. A disadvantage of the pressurized process is that both fuel gas and combustion air need to be compressed. (Häussinger et al. 2012)

Steam methane reforming with integrated hydrogen separation is also researched. High-temperature-resistant membranes are integrated in a tubular reformer to withdraw hydrogen after it is formed. This shifts the chemical equilibrium towards higher conversion of feedstocks. Palladium foil on a porous cylinder has been claimed suitable as a membrane. The process has only been tested in a laboratory-scale. (Häussinger et al. 2012)

5.1.4 Catalysts

Ni-based catalysts are used in SMR reactions because of their cheap price and availability. The catalysts usually contain 15–25 wt-% nickel oxide. Nickel oxide is reduced to metallic nickel with hydrogen, natural gas or the feed gas itself. (Liu et al. 2010, Häussinger et al. 2012)

Support is typically acidic aluminium oxide that favours hydrocarbon cracking and polymerization. Also aluminosilicates, cement and magnesia are used. Research is done to use promoters for modifying the Al_2O_3 support properties. For example, uranium oxide and chromium oxide can be used as promoters. Promoters have been reported to form less carbon and help the catalyst poison resistance of sulphur components. (Liu et al. 2010 & Häussinger et al. 2012)

Alternative supports have been investigated as well. $Ni-ZrO_2$ has performed better than $Ni-Al_2O_3$ especially at low reaction temperatures. MgO compared to Al_2O_3 promotes surface carbon gasification, which suppresses coke deposition. Ni-MgO has been stable in long-term tests. CeO_2 is also a popular support because of its oxygen storage capacity that prevents carbon formation. (Liu et al. 2010, Häussinger et al. 2012)

Noble metals have been studied to replace the carbon forming Ni-metal. Carbon does not dissolve in noble metals. Noble metals, Ru, Rh, Pd, Ir and Pt, have been tested in the SMR reaction. Ru and Rh achieved high reforming activities and low carbon formation rates. The problem of the noble metal use is however the cost and availability of them. (Liu et al. 2010)

5.2 Dry reforming

5.2.1 Overview of the process

The dry reforming reaction equation is the following (Halmann & Steinberg 1999, 317):

$$CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2 \tag{15}$$

$\Delta H_{298\,K} = 247$ kJ/mol

This reaction converts two inexpensive and widely used materials into valuable syngas. Dry reforming similarly to SMR requires temperatures above 700 °C for high conversion. Dry reforming was researched already by Fischer and Tropsch in

the 1920s. The best catalysts found were Ni supported on silica at 860 °C. (Halmann & Steinberg 1999, 317)

The dry reforming process is still only partly used along the steam methane reforming process. Some natural gas sources consist of more than 25% of CO_2. In these cases it is useful to let CO_2 directly react with CH_4. (Halmann & Steinberg 1999, 317)

There are some advantages of CO_2 reforming vs. SMR. The CH_4 amount in the end product is lower compared to SMR's 2% of unreacted methane. In some cases a lower H_2/CO ratio is also favoured compared to the SMR ratio of 3. One example is the oxo-synthesis to form aldehydes from alkenes (Häussinger 1990). Another example from these is the Fischer-Tropsch process, in which high H_2/CO ratios can suppress longer chain hydrocarbon growth and enhance methanation reaction. (Halmann & Steinberg 1999, 317)

5.2.2 Catalysts

As in SMR, also in dry reforming Ni-based catalysts achieve good activity together with relatively low price. However, higher carbon deposits and sintering makes them prone to deactivation. Noble metal catalysts such as Rh, Ru, Pd, Pt and Ir have also been tested. Especially Rh and Ru have shown high activity and stability. However, from the industrial point-of-view the cheaper non-noble metal catalysts are under a greater interest. Table 9 shows the results of different catalytic systems tested in methane dry reforming (Fan et al. 2009). (Ma et al. 2009)

Table 9. Catalytic systems tested in dry reforming of methane (Fan et al. 2009).

Catalyst	T (°C)	CH_4 conv. (%)	CO_2 conv. (%)	H_2/CO ratio	Coke formation
NiO/CaO	850	95	NA	1-2	NA
NiO/CaO	600-850	~100	NA	1.5-2.5	NA
NiO/CoO/MgO	800	>80	NA	1-2	NA
NiO/MgO/SA-5205	800	~90	88	1-2	NA
Mo_2C	847	92.4	92.5	0.93	NA
WC	847	92	93.1	0.94	
Ni/Al_2O_3	700	66	71	NA	
Ru/SiO_2	750	20	23	NA	16.4
Ru/Al_2O_3	750	35	39		19.5
Ru/MgO	750	39	44		1.2
Ru/TiO_2	750	28	30		NA
Ni/Al_2O_3	700	82.3	79	NA	
$Ni/Mo-Al_2O_3$	700	81.4	76.7		
Ni/Al_2O_3	800	67	73.7	0.93	
$Ni/0.2 \% Ca-Al_2O_3$	800	79.5	82.6	0.96	
$Ni/2 \% Ca-Al_2O_3$	800	69.2	76.1	0.92	
Ni/Al_2O_3	750	31.8	29.2	0.88	42.5
$Ni/MgAl_2O_4$	750	85.3	96.2	0.91	38.7
Co/SiO_2	600	41	64.5	NA	0.41
$Co/5 \% MgO-SiO_2$	600	42	65.3		0.29
$Co/35 \% MgO-SiO_2$	600	42.7	55.6		trace
$NdCoO_3$	850	~90	~90	~0.9	NA
Ni/Al_2O_3	800	82.9	82.9	NA	
$Ni/ZrO_2-Al_2O_3$	800	77.9	77.9		
$La_{1-x}Ce_xNiO_3$	750	50	50	0.43	NA
Ni/Al_2O_3	550	NA	NA	NA	7
$Ni/ZrO_2-Al_2O_3$	550	NA			0.9
Pt/Al_2O_3	550	NA			0.6
$Pt/ZrO_2-Al_2O_3$	550	NA	NA		0.1
$Ni-Cu/Al_2O_3$	750	15		0.96	0.002
$Ni-Fe/Al_2O_3$	750	55		1.00	0.023
$Ni-Mn/Al_2O_3$	750	85		0.94	0.006
$Ni-Co/Al_2O_3$	750	90		0.95	0.001
Ir/Al_2O_3	600	50	55	NA	NA
Ir/Al_2O_3	600	15	18		
Ni/SiC	750	92	93	1	NA

Research has been devoted towards a more stable Ni-based catalyst. MCM-41 (Figure 7) impregnated with Ni has been tested as well as Ni/SiC monolithic foam catalysts. The Ni/SiC catalyst performed particularly well. Ca^{2+} introduction with a Ni-based catalyst has been reported to improve the coke elimination capacity. A Ni-$CaO-ZrO_2$ catalyst has showed both high stability and activity in dry reforming laboratory tests.

5.3 Alternative process (electrolysis)

Electrolysis breaks water into pure hydrogen and oxygen with the following reactions occurring at electrodes, cathode reaction (16), anode reaction (17) and the whole reaction of the cell (18) (Häussinger et al. 2012).

$$2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq) \tag{16}$$
$$2OH^-(aq) \rightleftharpoons 1/2O_2(g) + H_2O(l) + 2e^- \tag{17}$$
$$H_2O(l) \rightleftharpoons H_2(g) + 1/2O_2(g) \tag{18}$$

where l = liquid, g = gaseous, aq = dissolved in water.

Figure 15 shows the principle of a water electrolysis cell.
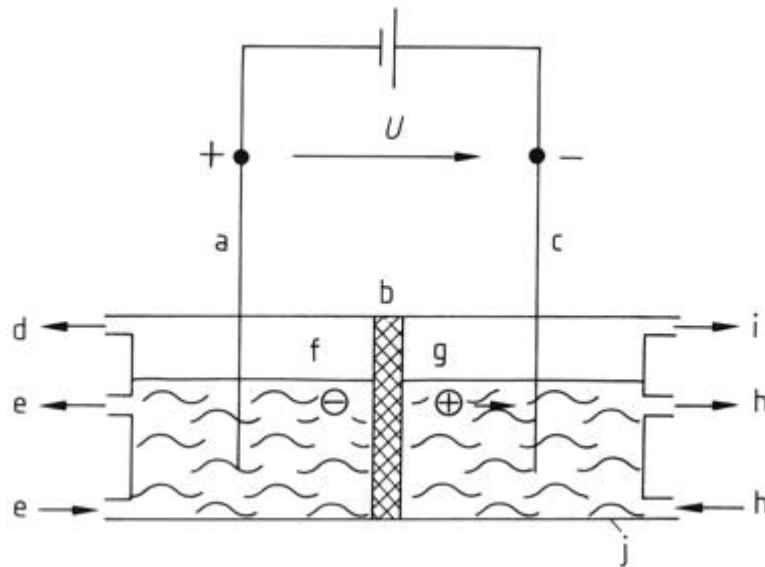
Figure 15. Schematic of a water electrolysis cell (Häussinger et al. 2012).

As seen from Figure 15, the process is very simple and produces pure hydrogen and oxygen. Temperature is usually at 70–90 °C. The advantage of the electrolysis process is the simplicity of operation but the electricity costs are too high if larger amounts of hydrogen are needed. (Häussinger et al. 2012)

6   Methanol synthesis

According to Fiedler et al. (2012) 70% of methanol is used in chemical syntheses of in the order of magnitude: formaldehyde, methyl *tert*-buthyl ether (MTBE), acetic acid, methyl methacrylate and dimethyl terepthalate. Energy production from methanol has only a small proportion of the total use but it has great future expectations (Mikkelsen et al. 2010).

6.1   Methanol synthesis via syngas

6.1.1 Overview of the process

The methanol synthesis from syngas takes place according to reaction (4). Also the CO_2 utilizing reaction (5) and the water gas shift reaction (6) have been reported to take place in the methanol synthesis via syngas (Kroschwitz 1995).

$$CO + 2H_2 \rightleftharpoons CH_3OH \tag{4}$$

$$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O \tag{5}$$

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \tag{6}$$

The modern methanol synthesis process was introduced by ICI in 1966. The process uses active Cu/ZnO catalysts. These catalysts can operate at temperatures from 250 °C to 300 °C and pressures from 50 to 100 atm – conditions that were significantly lower than in the previous processes (temperatures 300 to 400 °C and pressures 100 to 300 atm). (Lee, 1990)

Although methanol synthesis has thermodynamically a better conversion at high pressures, low pressures are favoured industrially. Some of the modern processes take place at pressures at which the methane steam reforming production of synthesis gas operates. The reason for this is synthesis gas compression being a costly operation and the overall energy consumption thus being lower in low-pressure processes. Lower temperatures than 200 °C would be the best choice thermodynamically, but catalysts require activation and reaction heat which is ensured with temperatures between 200–300 °C. Heat removal is very important in

this process because the reactions are highly exothermic. Figure 16 shows the ICI methanol production process. (Tijm et al. 2001, Fiedler et al. 2012)
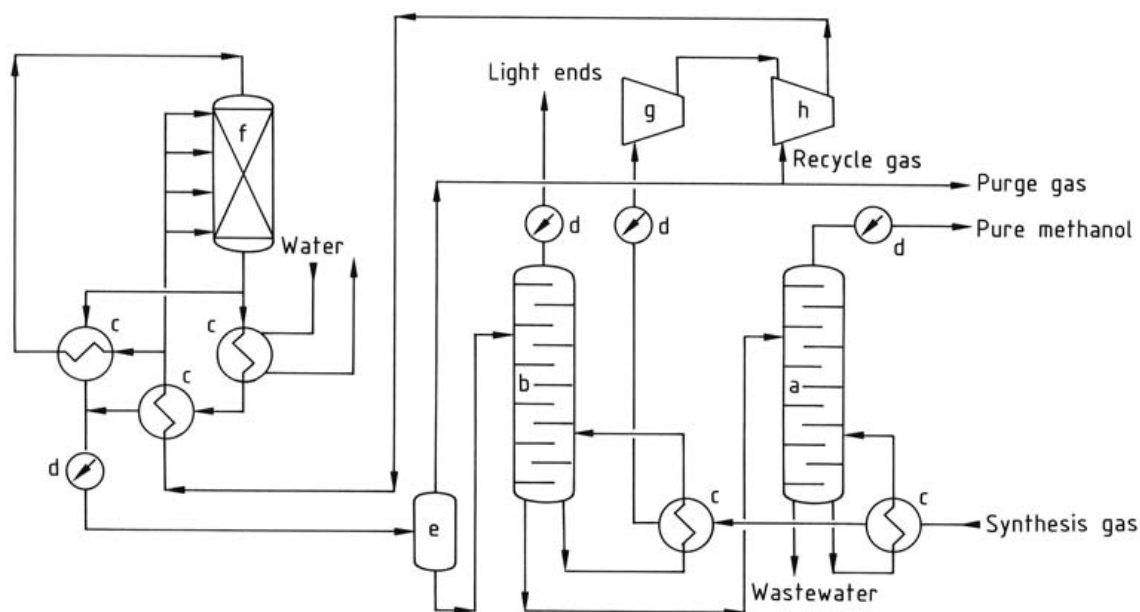
Figure 16. ICI methanol process a) Pure methanol column, b) Light ends column, c) Heat exchanger, d) Cooler, e) Separator, f) Reactor, g) Compressor, h) Compressor recycle stage (Fiedler et al. 2012).

As Figure 16 shows, crude methanol is purified with two distillation columns. The light ends column (b) separates impurities having a low boiling point. The pure methanol column (a) separates heavier products and water. The heat exchanger (c) transfers energy from the reacted gas to the feed gas. Feed gas is colder because the reaction (f) is exothermic. After the heat exchanger the reacted mixture is further cooled (d). (Fiedler et al. 2012, Poels & Brands 2002)

Methanol is separated from the product gas in a separator (16e). The recycle compressor is used to pressurize the unreacted gas. Other compounds are mixed with fresh syngas to compress and react again (h). A small percentage of the gas leaving the separator is continuously purged in order to prevent inert gases from building up in the synthesis loop (N_2 and CH_4). The product flow contains 4–8% methanol. (Fiedler et al. 2012, Poels & Brands 2002)

6.1.2 Reactors

Different converter types are used in methanol synthesis (Figure 17) (Novak & Lesko 1995).
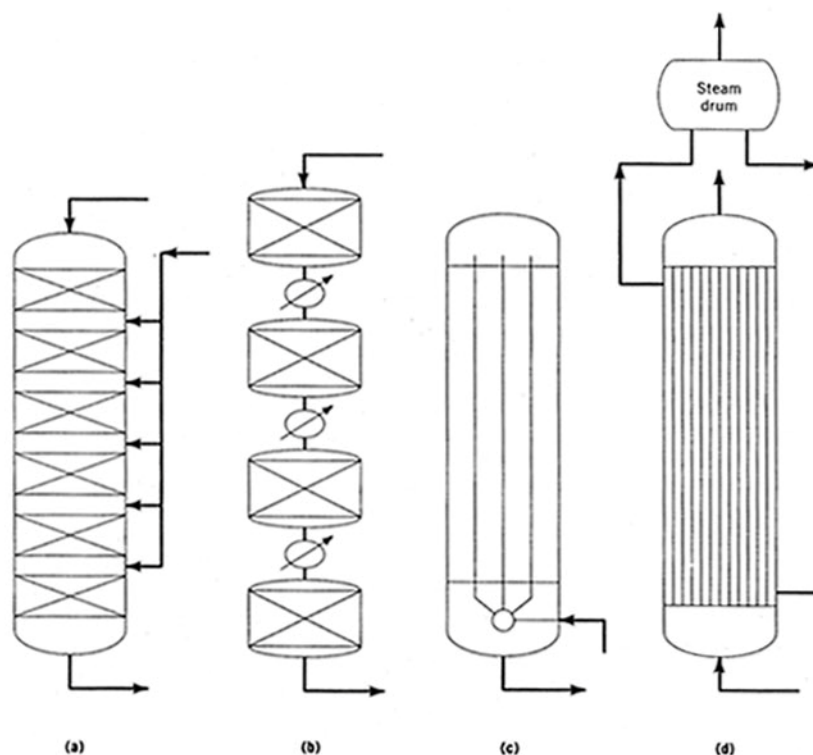
Figure 17. Methanol converter types: (a) quench, (b) multiple adiabatic, (c) tube-cooled, and (d) steam-raising (Novak & Lesko 1995).

The quench converter is the type of an ICI-reactor. Syngas-recycle gas-mixture is fed to the intermediate catalyst beds. Remaining gas is fed into the first bed. Beds are adiabatic which means that the gas temperature increases as the exothermic reactions proceed. Injection of lower temperature quench gas between the beds cools the mixture and provides new reactants. Quench converters usually contain three to six catalyst beds. Between each bed there is a gas distributor for the quench gas. An adiabatic converter uses the same principle but employs heat exchangers for the cooling. A detailed picture of one of the ICI reactor is shown in Figure 18. (Novak & Lesko 1995)
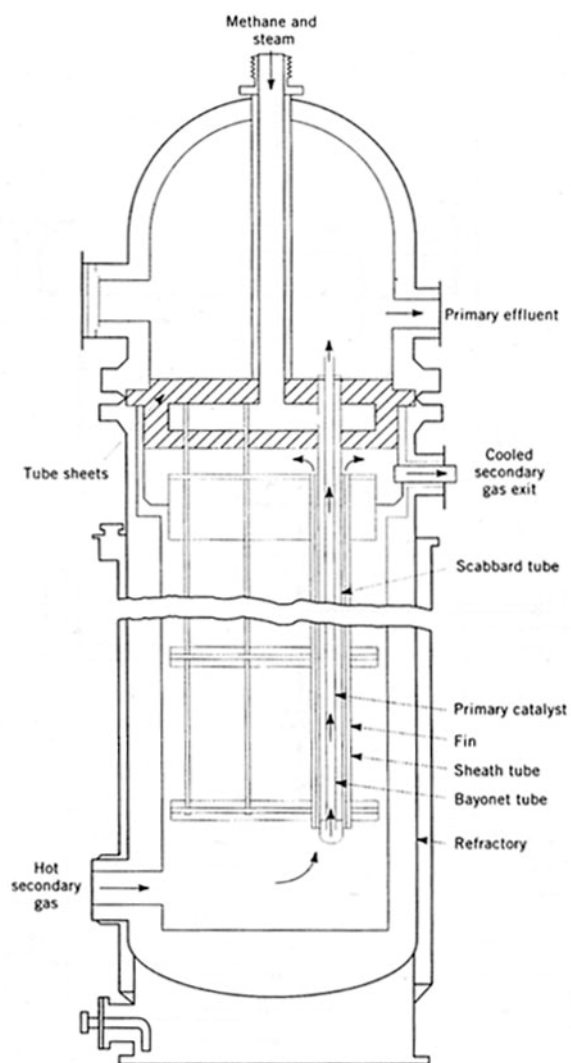
Figure 18. ICI design for the methanol synthesis reactor (Novak & Lesko 1995).

The tube-cooled converter consists of a tube-filled vessel with the catalyst on the shell side. Recycled gas and syngas are fed from the bottom of the reactor tubes and heated by the reaction taking place in the surrounding catalyst bed. The advantage of the tube cooled converter is the reduction in catalyst volume. (Novak & Lesko 1995)

The steam-raising converter can feature radial or axial flow with the catalyst either on the shell or tube side. This kind of a reactor is quasi-isothermal and the most thermodynamically efficient of the types used and thus requiring the least catalyst volume of different converter types. (Novak & Lesko 1995)

Modern commercial methanol synthesis processes are based entirely on heterogenous systems like the ICI and the Lurgi processes. According to Fiedler (2012), the ICI-process (adiabatic reactor) accounts for 60%, and the Lurgi-process (quasi-isothermal reactor) for 30% of annual production of methanol in the world.

6.1.3 New developments in reactor technologies

The modern converter technology is the three-phase (gas-solids-liquid) technology. Also "liquid-phase" is used as the name for the new technology. This technology allows methanol to be removed from the reactor by a liquid as an absorbing medium. Also the heat management is improved. Pulling the methanol out of the equilibrium reaction, the technology aims to avoid the problems of low conversion and the need for high recycle rates found with conventional fixed bed methods. (Tijm et al. 2001)

One promising liquid-phase process is LPMEOH^{TM} by Air Products. This process uses existing methanol catalysts in a fine powder form, suspended in an inert mineral oil. The mineral oil acts as a temperature moderator and heat removal medium. The heat of reaction is efficiently transferred from the catalyst surface to boiling water in an internal tubular heat exchanger. The reactor therefore has more efficient heat transfer which allows a constant temperature to be maintained in the converter. Therefore a higher conversion is achieved and the number of recycle passes is reduced. The gas phase process operates usually with the 5:1 recycle ratio when the liquid process operates fine with the ratios of 1:1 to 2:1. (Tijm et al. 2001)

Brookhaven laboratory in NY, USA has developed a methanol synthesis process that operates in lower process conditions than conventional processes. The process uses a homogenous liquid phase systems and claims conversion rates in excess of 90 %. This means also that no syngas recycling is needed. The low pressure operation together with the inertness of the catalyst to N_2 allows partial oxidation of natural gas by air, eliminating the need for air separation during the syngas manufacture. (Tijm et al. 2001)

6.1.4 Catalysts

The current ICI catalyst is composed of copper oxide and zinc oxide on a carrier of aluminium oxide. The ratios of the components vary as CuO ranges between 40 and 80%, ZnO between 10 and 30% and Al_2O_3 from 5 to 10%. Additives such as MgO may also be added. Synetix (former ICI), Süd Chemie, Haldor Topsoe and Mitsubishi Gas Chemical are the biggest methanol synthesis catalyst manufacturers. The life of the catalyst can be up to 4 years (Lee, 1990, Tijm et al. 2001)

Synetix developed a catalyst in the 1990's that limits sintering with added MgO. Synetix also claims that this catalyst has 30 % higher copper surface area than other catalysts. This catalyst also prevents the formation of CO_2. (Tijm et al. 2001)

Süd Chemie has argued that high CO_2 levels are a result of water formation in the synthesis reaction. They therefore developed two new methanol catalysts that have a higher tolerance of carbon oxides (CO and CO_2) and are designed to show an optimum balance between the activity, selectivity and lifetimes as plant sizes increase. Süd Chemie has also different catalysts depending on the source of syngas (partial oxidation vs. SMR). (Tijm et al. 2001)

Haldor Topsøe produced a multi-purpose catalyst that gained industrial experience with most types of converters using syngas from different sources. Topsøe has reported that the same catalyst has been used also in an ammonia methanol co-production unit. (Tijm et al. 2001)

Methanol conversion from CO and H_2 of almost 50% per pass compared to the 10 % of the conventional methods has been claimed by researchers at the Central Research Institute of the Electric Power Institute (Tokyo). The catalyst which includes alkali metal alkoxide, chromium and copper oxides works at 200–300 °C and less than 50 bar. The catalyst has an amorphous structure and very fine particles which allow higher yields.

6.2 Methanol synthesis via CO$_2$

6.2.1 Overview of the process

Methanol synthesis via CO$_2$ proceeds via the route shown in Equation 19:

$$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O \hspace{4cm} (19)$$

According to Fiedler et al. (2012) some researchers have gotten results of methanol formation happening solely via carbon dioxide route in the same process conditions as the syngas route. Isotope-labelled reactants show that both reaction pathways are possible and some studies have shown that formation via carbon dioxide predominates under conditions of large-scale industrial methanol synthesis. There are also studies that show no production of methanol if the CO/H$_2$ mixture is carefully purified from CO$_2$ (Olah et al. 2009).

6.2.2 Catalysts

Finding suitable catalysts for methanol synthesis via CO$_2$ is an interesting area for catalyst research. Especially copper based catalysts have been widely studied together with various metal oxides such as Al$_2$O$_3$, Cr$_2$O$_3$, TiO$_2$, ZnO and ZrO$_2$ and their combinations. A copper based catalyst together with zirconia has been reported being especially active in terms of CO$_2$ conversion. Copper catalysts have performed better than Ag and Au catalysts in terms of activity. However, in selectivity the noble metals have gotten better results as seen from Table 10. Table 10 shows various catalytic systems that have been tested in the CO$_2$ route of methanol synthesis gathered by Yang et al. 2011. (Raudaskoski et al. 2007)

Table 10. Catalytic systems tested in the CO_2 route of methanol synthesis (Yang et al. 2011).

Catalyst	Preparation method	T/°C	CO_2 conversion (%)	Methanol selectivity (%)
$Cu/Zn/Ga/SiO_2$	co-impregnation	270	5.6	99.5
$Cu/Ga/ZnO$	co-impregnation	270	6.0	88.0
Cu/ZrO_2	deposition-precipitation	240	6.3	48.8
$Cu/Ga/ZrO_2$	deposition-precipitation	250	13.7	75.5
$Cu/B/ZrO_2$	deposition-precipitation	250	15.8	67.2
$Cu/Zn/Ga/ZrO_2$	coprecipitation	250	n/a	75.0
$Cu/Zn/ZrO_2$	coprecipitation	250	19.4	29.3
$Cu/Zn/ZrO_2$	urea-intrate combustion	240	17.0	56.2
$Cu/Zn/ZrO_2$	coprecipitation	220	21.0	68.0
$Cu/Zn/ZrO_2$	glycine-nitrate combustion	220	12.0	71.1
$Cu/Zn/Al/ZrO_2$	coprecipitation	240	18.7	47.2
$Ag/Zn/ZrO_2$	coprecipitation	220	2.0	97.0
$Au/Zn/ZrO_2$	coprecipitation	220	1.5	100
$Pd/Zn/ZrO_2$	incipient wetness	250	6.3	99.6
G_2O_3-Pd/SiO_2	incipient wetness	250	n/a	70.0
$LcCr_{0.5}Cy_{0.5}O_3$	sol-gel	250	10.4	90.8

As seen from Table 10, Cu is the dominant metal in the research of methanol synthesis via CO_2. It also leads to the best conversions of CO_2 although methanol selectivity is not the best. Promoters such as Si, Ti, Al, Zn, Zf and Ce have been used together with Cu. Temperature and pressure can be lowered with promoters. For example the $Cu/ZnO/M_2O_3$ catalyst works at pressure of 10 bar compared to the normal methanol synthesis pressure of 50 bar. (Liu et al. 2003)

7   Carbonate production (DMC synthesis)

DMC synthesis is used industrially as an alternative to phosgene for polycarbonate and isocyanate syntheses. The product DMC can be used as methylation agent and as a solvent. The future use might be as a fuel compound to replace MTBE (Keller et al. 2010).

7.1   Oxydative carbonylation route

7.1.1 Overview of the process

Most of the world's DMC production is done with the oxidative carbonylation route patented by EniChem in 1980 (Pachecho & Marshall 1997). In the reaction methanol, CO and oxygen react in a CuCl-slurry catalyst system (20). (Fukuoka et al. 2003)

$$2CH_3OH + CO + \tfrac{1}{2} O_2 \rightleftharpoons (CH_3O)_2CO + H_2 \qquad\qquad (20)$$
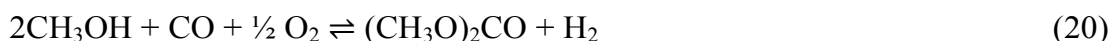
The process conditions in the EniChem route are typically 20–30 atm and 100–130 °C according to Pachecho et al. (1997). Another carbonylation route was later introduced by UBE Industries – a Japanese chemical company (UBE Industries, Ltd. 2012). This process takes place in two steps and in gas-phase. The first phase includes a reaction of methanol with nitrogen oxides and oxygen to give methylnitrite and water. This reaction is conducted without a catalyst and at 50 °C. In the second reaction methylnitrite reacts with carbon monoxide to produce dimethylcarbonate. This reaction is run at 100–120 °C and 5–10 bars over a palladium supported catalyst in a fixed bed reactor. An assumed process sheet of the EniChem process is shown in Figure 19. (Delledonne et al. 2001)
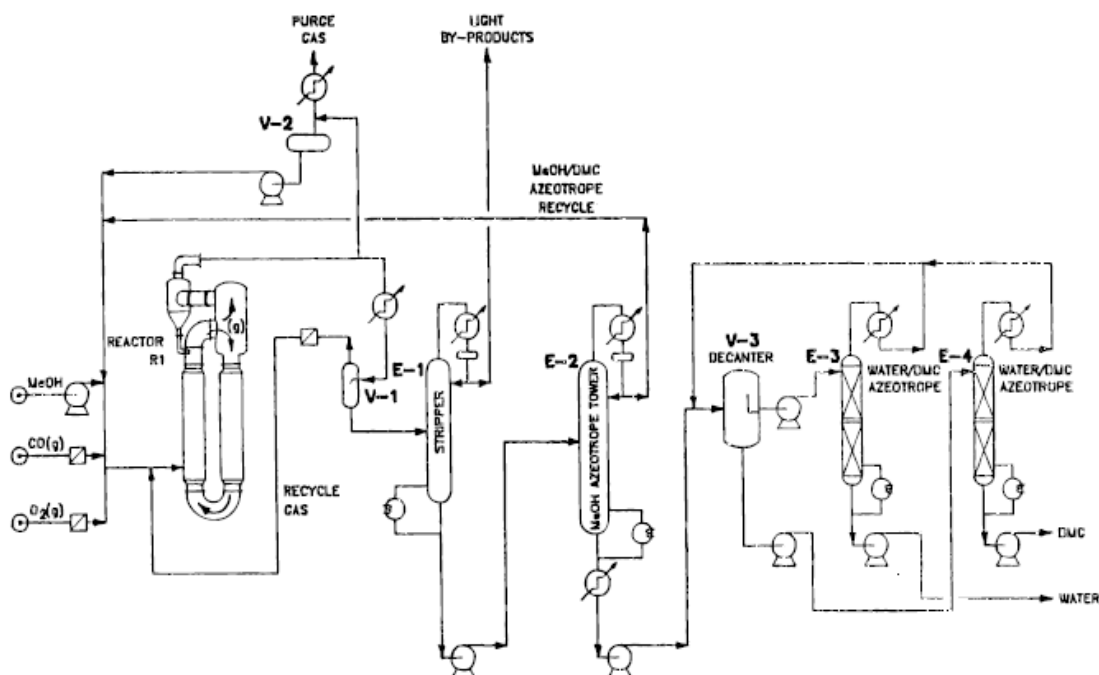
Figure 19. Shematic process sheet of the EniChem DMC production process (Pachecho & Marshall 1997).

The EniChem process illustrated in Figure 19 achieves a DMC selectivity of 65-70 %, which is based on more than 95% used CO and MeOH. 30% by-production of CO_2 is unavoidable. Due to HCl, high concentrated CuCl-slurry and the water produced the process has been reported being corrosive. The produced DMC contains chloride impurities derived from the catalyst system. These impurities are rather difficult to separate. Even very small amounts (less than 0.1 ppm) of chloride impurities can have bad effects on the polymerization reaction and on the performance of the DMC produced. Energy consuming and DMC yield lowering separation processes need to be added to the process. Water as one of the end products must be separated from the reaction mixture and treated before disposal (Fukuoka et al. 2007, Fukuoka et al. 2003).

7.1.2 Reactors

The EniChem process uses a slurry reactor that is shown together with a simplified flow diagram in Figure 20 (Keller et al. 2010).
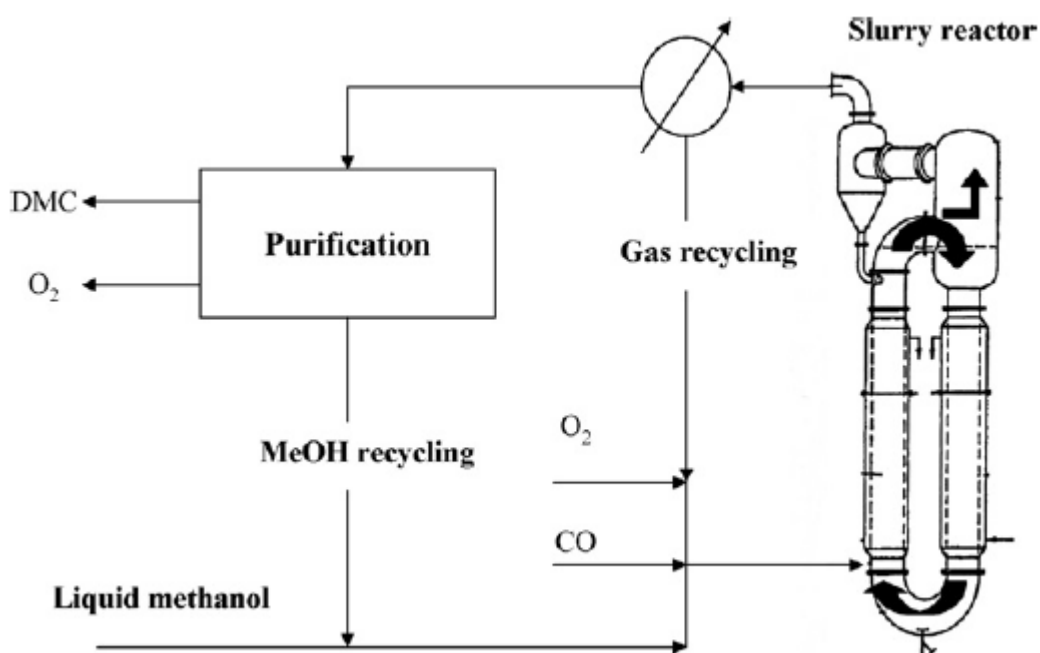
Figure 20. Schematic process sheet of the EniChem carbonylation process with the slurry reactor (Keller et al. 2010).

In the scheme shown in Figure 20 two tall vertical cylindrical slurry vessels are connected at the top and bottom. Feedstock gases enter from the bottom of the first vessel and lift the slurry relative to the second vessel. A density difference is created. More dense slurry circulates from the bottom of the second vessel into the reactor. At the same time less dense slurry is fed to the other vessel from the top of the reactor. The other reactor effluent is withdrawn from the top of the two vessels through a cyclone. There can be only one reactor or several slurry reactors in series. MeOH and CO are only partly converted. Oxygen (or air) is the limiting reagent and cannot be present in the system much above 4 mol-% to avoid the potential for explosion wherever CO is the main gas phase component. (Pachecho & Marshall 1997)

7.1.3 *New developments in the reactor technology*

EniChem produced a novel process design to eliminate the need for solid-liquid separations outside the reactor itself. This is done with vaporizing or stripping some the reactor contents. Vapour outside the reactor is condensed. Uncondensed vapour is recycled back to the reactor. A small amount of HCl is added into the reactor to maintain a proper Cu/Cl ratio in the reactor. (Pachecho & Marshall 1997)

7.1.4 Catalysts

A halide-free, non-corrosive catalyst is being researched. Cobalt(II) complexes with NO ligands such as carboxylates and acetylacetonates have achieved good activity in DMC formation (Cavani et al. 2009). Schiff base ($R^1R^2C=NR3$) with Co achieved good selectivity (greater than 96%) but the overall production of DMC lowered (Pachecho & Marshall 1997).

7.2 CO$_2$ route

The direct synthesis of DMC was studied already in the 1980's by Hoffmann (1982). The reaction is shown in Equation 20:

$$2CH_3OH + CO_2 \rightleftharpoons (CH_3O)_2CO + H_2O \qquad\qquad (20)$$

Because no commercial plant using this reaction exists, the process technology review is made for a polycarbonate producing CO_2 utilizing process. A CO_2 utilizing full-production plant of polycarbonate has been operating since June 2002. The factory is a joint venture between Asahi Kasei Corporation and Chi Mei Corp. High yield and high selectivity of carbonate is claimed in both production steps, the monomer and polymer production steps. (Fukuoka et al. 2007)

7.2.1 Overview of the process (Asahi Kasei polycarbonate process)

Overview of the two basic reactions in the Kasei process are shown in Figure 21 (Fukuoka et al. 2010).
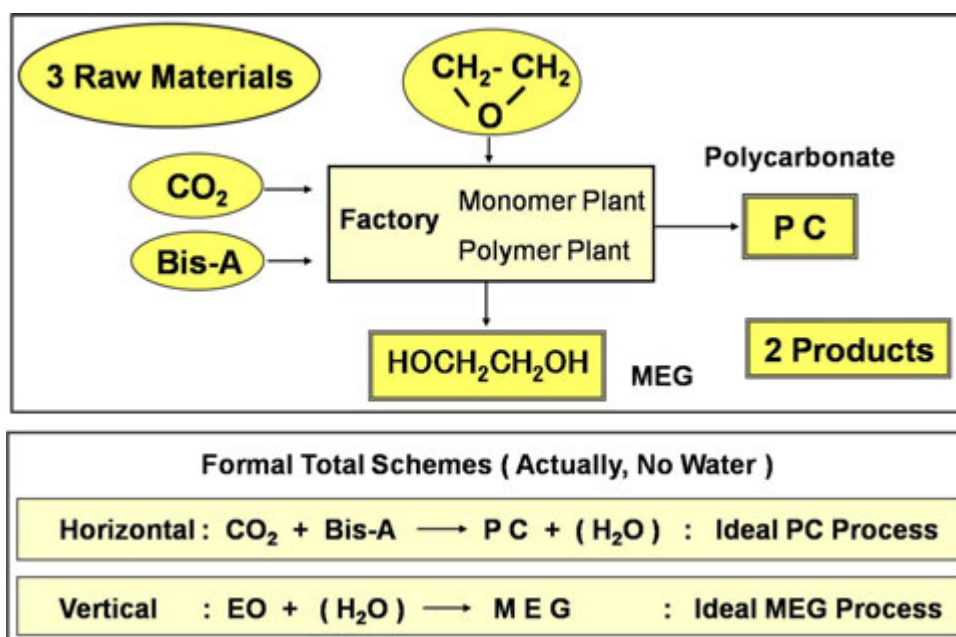
Figure 21. The Asahi Kasei's process (Fukuoka et al. 2010).

As Figure 21 shows, the three raw materials react in two reactors to produce polycarbonate and monoethyleneglycol. This process has some advantages compared to the conventional EniChem route. Process water does not need to be used. The CO_2 used in the process is a by-product from the production of ethylene oxide. Ethylene oxide is used usually to make ethylene glycol for PET bottles, films and fibres, etc. In its normal production process CO_2 is released to the atmosphere. All of the intermediates, ethylene carbonate, dimethyl carbonate, methanol, diphenyl carbonate and phenol are entirely used or recycled. Because of no process water is used, monoethylene glycol (MEG) can be selectively manufactured in high yields by the energy-saving process. Purification and separation are also claimed not necessary in this process. (Fukuoka et al. 2007 & 2003)

7.2.2 Reaction (Direct synthesis of DMC)

The major problems with DMC synthesis via CO_2 are the decomposition of the catalyst and hydrolysis of the formed carbonate. If the direct synthesis of DMC (18) is commercialized in the future, if is probable that the process uses a drying agent together with a catalyst. Figure 22 shows the advantages that this kind of reaction provides. (Sakakura & Kohno 2009)
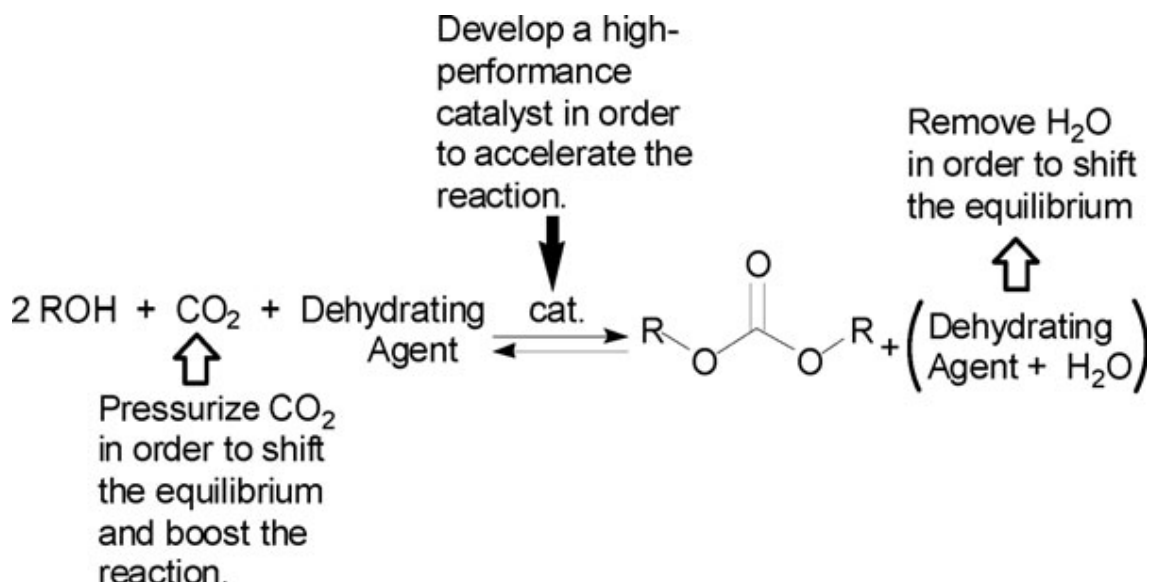
Figure 22. Direct DMC synthesis reaction with arrows for pointing the parts where developments need to be done (Sakakura & Kohno 2009).

As presented in Figure 22, CO_2 compression can give a boost to the reaction. Drying agents make the reaction more favorable for DMC formation. The drying agent can be non-recyclable or recyclable. Non-recyclable includes dicyclohexal carbodiimide (DCC) orthoesters (orthoacetate, $Si(OMe)^4$) and Mitsunobo reagent. Recyclable agents include acetals and molecular sieves. A schematic diagram of direct DMC synthesis using MS 3A as a recyclable drying agent is shown in Figure 23 by Sakakura & Kohno (2009).
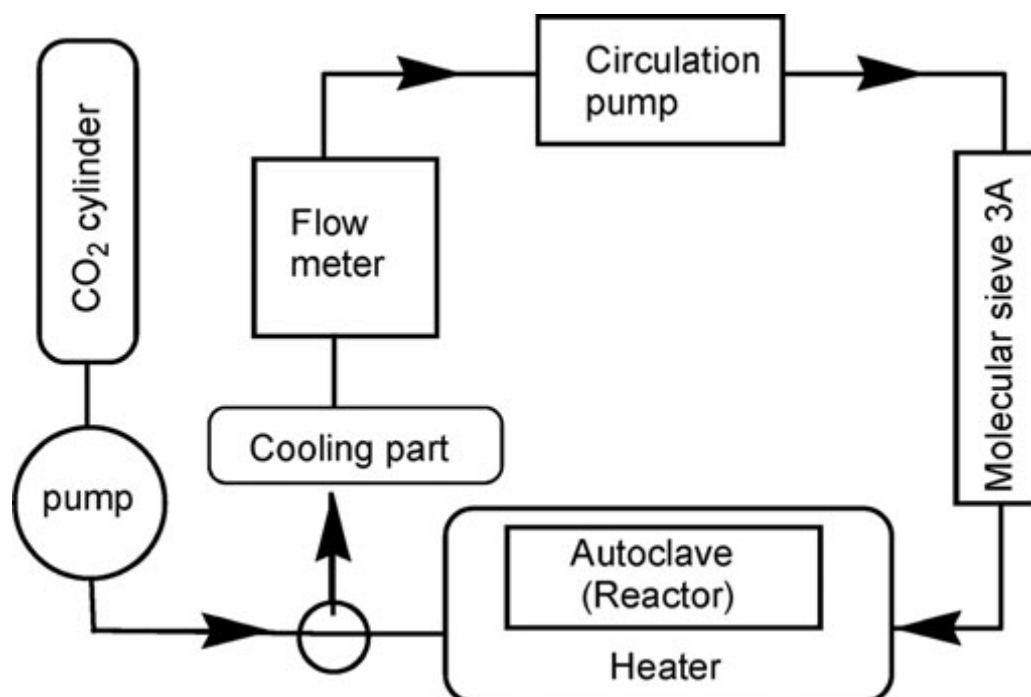
Figure 23. Schematic diagram of the direct DMC synthesis using MS 3A as the recyclable drying agent (Sakakura & Kohno 2009).

7.2.3 Catalysts (Direct synthesis of DMC)

Catalytic systems of DMC synthesis via CO_2 have been studied for a long time. Table 11 shows the results from various references for the DMC synthesis by dehydrative condensation of CO_2 (Sakakura & Kohno 2009).

Table 11. Results from different research systems of DMC synthesis via CO_2. Gathered by Sakakura & Kohno (2009).

Catalyst	Dehydrating agent	Conditions	DMC yield based MeOH	Reference year
$Bu_2Sn(OMe)_2$	Acetal (2,2-dimetxoypropane)	180 °C, 300 bar	6 %	1999–2000
	MS3A[a]	180 °C, 72h, 300 bar	45 %	2002
	Acetal[a]	180 °C, 24h, 300 bar	40 %	2008
ZrO_2	None	100 °C, MeOH:CO_2 = 1:3	1 %	1999
ZrO_2+HPO_4	None (self cat.)	130 °C, MeOH:CO_2 = 0.99:1	0.62 %	2000
ZrO_2+CeO_2	None (self cat.)	110 °C MeOH:CO_2 = 0.2:1	1.6 %	2002
ZrO_2+CeO_2	Acetal[a]	130 °C, 140h MeOH:CO_2 = 0.99:1	4.3 %	2002
$Ni(OAc)_2$	None (self cat.)	140 °C, 74 bar	2.1 %	2000
$Nb(OR)_5$	None (self cat.)	137 °C, 30h, 55 bar	2 %	2003
H_3PO_4 + V_2O_5	None (self cat.)	140 °C MeOH:CO2 = 1:0.5	1.8 %	2005
CuCl + MeOC(O)ONa	DCC	65 °C, 24h, 50 bar	0.8 %	2005
Cu-Ni + VSO	None (self cat.)	180 °C, MeOH:CO2 = 1:0.5	2.6 %	2006
$Cu1,5PMo_{12}O_{40}$ (heteropolyacid)	None (self cat.)	50 °C, 1.2 bar	1.6 %	2006
$H_3PW_{12}O_{40}$ + Ce-Ti-O	None (self cat.)	170 °C, 12h, 50 bar	5 %	2006
Cu-Ni/VSO photoirradiation	None (self cat.)	120 °C, UV irradiation	4 %	2007
$Ti(OMe)_4$ + acid	Acetal[a]	180 °C, 24h, 300 bar	24 %	2008
$Ti(OMe)_4$ + polyether	Acetal[a]	180 °C, 24h, 300 bar	55 %	2008
Mg	None (self cat.)	180 °C, 12h, 150 bar	1 %	2008

A=recyclabe

As seen from Table 11, the yield of DMC changes a lot between the reference years although the same catalyst is used. It is also seen that temperatures in all tests are rather low (less than 200 °C) but pressures are in many tests as high as 300 bar.

7.3   Alternative process (phosgenation)

Keller et al. (2010) stated that the phosgene route to produce carbonates was implemented by Bayer AG in 1958. For the DMC production the phosgenation reaction passes through a methylchloroformate intermediate (21).

$$COCl_2 + CH_3OH \rightleftharpoons ClCOOCH_3 + HCl \qquad (21)$$

The produced methylchloroformate ($ClCOOCH_3$) reacts after this with methanol to give DMC and HCl as the end products (22) (Keller et al. 2010).

$$ClCOOCH_3 + CH_3OH \rightleftharpoons (CH_3O)_2CO + HCl \qquad (22)$$

In the process the chloroformate and methanol are fed continuously into a Raschig ring-packed column in which a temperature gradients of 72–127 °C is maintained between the head and the base of the column. HCl is withdrawn from the head and 99 % carbonate from the base. (Pachecho & Marshall 1997)

The process can be performed at as low temperatures as 0 °C with toluene or dichloromethane solvents in the presence of pyridine excess to shift the reaction equilibrium towards DMC formation. If the process is chosen to produce polycarbonates, methanol is changed into Bis-A. The process for polycarbonate production is shown in Figure 24. (Keller et al. 2010)
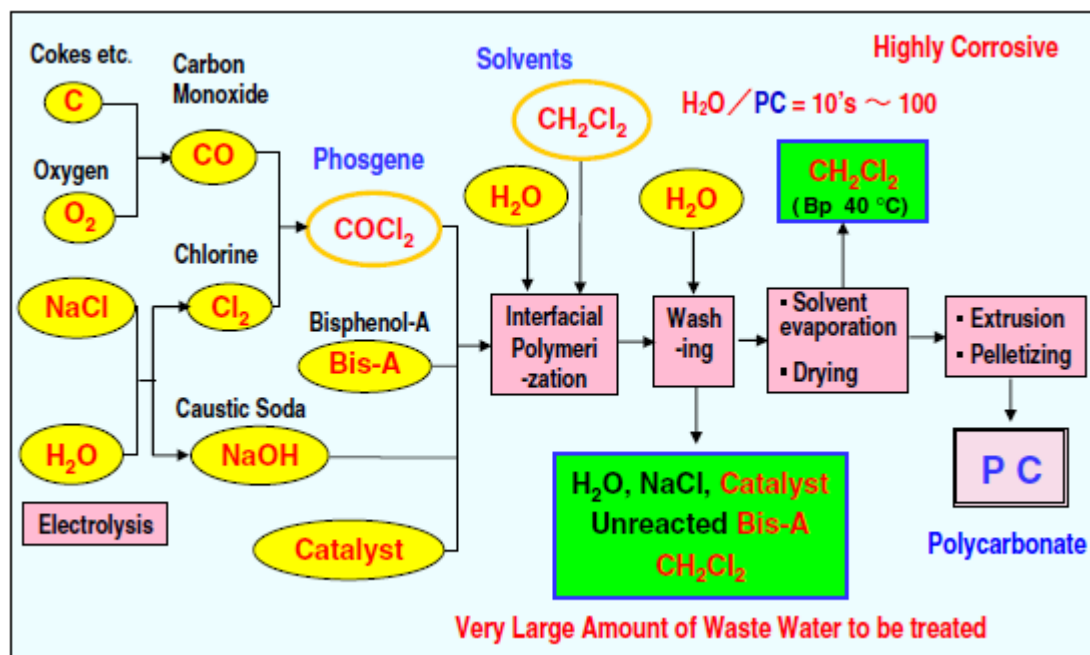
Figure 24. Phosgene route for the PC production (Fukuoka et al. 2007).

The process shown in Figure 24 is for polycarbonate production. As the process sheet shows, the reaction is rather complex. If the process is chosen to produce DMC, methanol takes Bis-A's place as one of the raw materials. The phosgene route has several environmental drawbacks that make it an undesirable process. The process has to use the very hazardous phosgene as a monomer. It also uses methylene chloride CH_2Cl_2 as a polymerization solvent. Methylene chloride has a low boiling point with an exposure limit that reflects its carcinogenic properties. Low boiling point also makes it release easily to atmosphere. Phosgene route also needs cleaning of large quantities of wastewater as methylene chloride is soluble in water. Also reactors, lines, pumps and valves need to be corrosion-resistant due to hydrochloric acid and aqueous solution of NaCl produced. (Fukuoka et al. 2007)

8 Sustainability assessment as a tool for engineers

8.1 Definition of sustainability

Sustainable development is development that meets the needs of present without compromising the ability of future generations to meet their own needs. Another clarification is a consideration of three impact areas, environmental, economic and social responsibility. Sustainability can be thus considered as social and environmental performance together with the conventional concept of financial performance. (Harmsen & Powell 2010)

8.2 Practical tools for process industries

Sustainability evaluation of a process includes evaluation of the environmental, social and economic impacts of a process. Examples of some of these impacts are listed in Table 12 (Azapagic et al. 2002).

Table 12. Examples of impacts on sustainability (Azapagic et al. 2002).

Environmental		Social	Economic
Resources	Emissions		
Material	Atmospheric impact	Health and safety	Value
Land	Impact to land	Society	Investment
Energy	Aquatic impact	Employments	Profit
Water		Workplace	Tax

There are many ways to evaluate the sustainability of a process. Some of them are direct tools that work well only on an existing process. Some, such as Green Chemistry, are more approaches than direct tools. (Harmsen & Powell 2010)

8.3 Green Chemistry

The concept of Green Chemistry was introduced in the early 1990s in USA. The aim was to "promote innovative chemical technologies that reduce or eliminate the use or generation of hazardous substances in the design, manufacture and use of chemical products". Green Chemistry is a culture and a methodology to achieve

more sustainable processes. The twelve principles of Green Chemistry are shown in Table 13. (Harmsen & Powell 2010, Anastas & Warner 1998)

Table 13. The principles of Green Chemistry (Anastas & Warner 1998, 30).

Principle	Explanation
1. Waste prevention	It is better to prevent waste than to treat or clean up waste after it has been created.
2. Atom economy	Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
3. Less hazardous chemical synthesis	Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment.
4. Designing safer chemicals	Chemical products should be designed to affect their desired function while minimizing their toxicity.
5. Safer solvents and auxiliaries	The use of auxiliary substances (e.g., solvents, separation agents, etc.) should be made unnecessary wherever possible and innocuous when used.
6. Design for energy efficiency	Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure.
7. Use of renewable feedstocks	A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.
8. Reduce derivatives	Unnecessary derivatization (use of blocking groups, protection/ deprotection, temporary modification of physical/chemical processes) should be minimized or avoided if possible, because such steps require additional reagents and can generate waste.
9. Catalysis	Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
10. Design for degradation	Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment.
11. Real-time analysis for Pollution Prevention	Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.
12. Inherently Safer Chemistry for Accident Prevention	Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires.

8.4 Green Chemistry metrics

Green Chemistry uses notably different metrics than conventional industrial chemistry (Harmsen & Powell 2010). In this thesis yield and atom economy are

used although according to Constable et al. (2002) yield is not a green chemistry metrics. However in a conceptual process development it is more suitable to be used than the typical green chemistry metrics such as mass intensity, carbon efficiency and reaction mass efficiency.

8.4.1 Yield

As Himmelblau & Riggs (2004, 241) have reported, yield has no universally agreed definition. Instead there are at least three common definitions for yield:

- **Yield based on feed** = the amount (mass or moles) of desired product obtained divided by the amount of the key reactant fed;
- **Yield based on reactant consumed** = the amount (mass or moles) of desired product obtained divided by the amount of the key reactant consumed;
- **Yield based on theoretical consumption of the limiting reactant** = the amount of a product obtained divided by the theoretical amount of the product that would be obtained based on the limiting reactant in the chemical reaction equation if it was completely consumed.

In this thesis the yield based on feed and yield based on reactant consumed are feasible to calculate.

8.4.2 Atom economy

Constable et al. (2002) have stated that when developing chemical processes chemists focus mainly on maximizing selectivity and yield. However, in recent years the term of atom economy introduced by Barry Trost has gained attention within the scientific community. Atom economy in nutshell shows the amount of reactants in the final product. For a reaction

$$A + B \rightarrow C \tag{23}$$

Atom economy $= (M_C) / (M_A + M_B) \times 100$

$(M_i$ = molecular weight of compound i)

The calculation includes only the reactants used. Intermediates that are produced and consumed in the reactions are ignored. This means that it is not possible to multiply the atom economy of each stage to give the total atom economy. Process atom economy is therefore calculated in the following way (Constable et al. 2002):

$$A + C \rightarrow C \tag{24}$$
$$C + D \rightarrow E \tag{25}$$
$$E + F \rightarrow G \tag{26}$$

Atom economy = $(M_G) / (M_A + M_B + M_D + M_F)$

Experimental part

9 Aim, procedure and methods in the empirical part

9.1 Aim of the empirical part

The aim of the experimental part was to compare the material and energy balances, economics and sustainability of the selected CO_2 utilizing processes and the corresponding conventional processes. The selected processes were syngas production (methane steam reforming vs. dry reforming), methanol synthesis (syngas route vs. CO_2 route) and DMC manufacture (oxidative carbonylation route vs. CO_2 route). The selected three CO_2 utilizing reactions and the corresponding conventional reactions are shown in Table 14.

Table 14. Cases examined in the empirical part.

Product	Conventional reaction	CO_2 utilizing reaction
Syngas	Steam methane reforming: $CH_4 + H_2O \rightleftharpoons 3H_2 + CO$	Dry reforming: $CH_4 + CO_2 \rightleftharpoons 2H_2 + 2CO$
Methanol	Methanol synthesis: $2H_2 + CO \rightleftharpoons CH_3OH$	Methanol synthesis via CO_2: $3H_2 + CO_2 \rightleftharpoons CH_3OH + H_2O$
DMC	Oxydative carbonylation: $2CH_3OH + 1/2O_2 + CO \rightleftharpoons C_3H_6O_3 + H_2O$	DMC synthesis via CO_2: $2CH_3OH + CO_2 \rightleftharpoons C_3H_6O_3 + H_2O$

The selected processes shown in Table 14 are all promising options for large scale CO_2 chemical utilization. They also have corresponding conventional processes which can be easily compared to the CO_2 utilizing process in the empirical part.

9.2 Procedure

A schematic of the procedure used in the empirical part of the thesis is depicted in Figure 25.
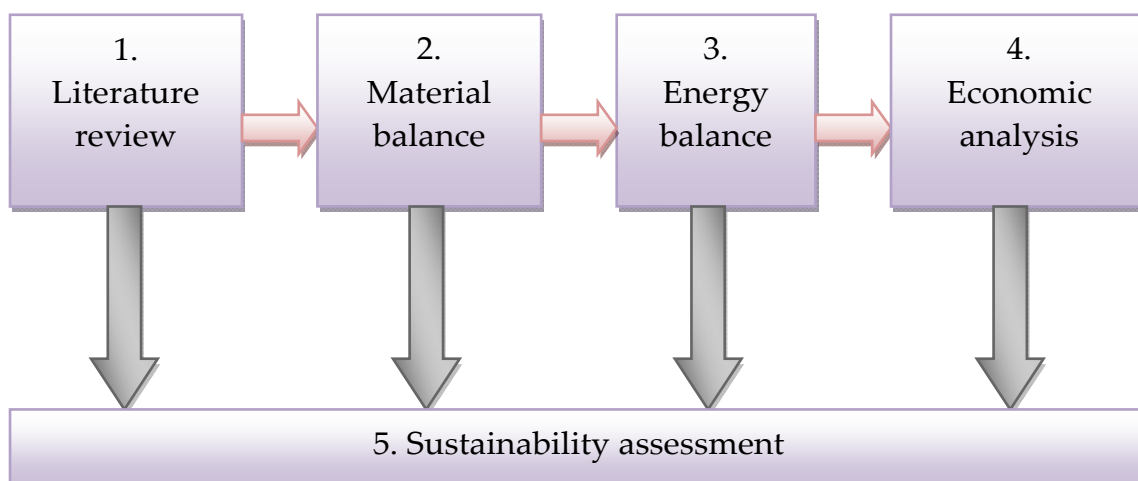
Figure 25. Schematic of the procedure used in the empirical part.

As Figure 25 shows, material and energy balances were calculated based on process conditions gathered from the literature reviews and the thermodynamic calculations. Thermodynamic calculations were carried out with HSC Chemistry and Aspen Plus. Economic analysis was done based on the thermodynamic analysis results. The total costs of the processes were evaluated with different CO_2 tax costs and different CO_2 separation costs. Sustainability assessment was done based on all the previous information.

9.3 Methods

At the stage of conceptual chemical process development a pure thermochemical approach is considered to be enough for making decisions. Therefore in this study only thermochemical equilibria are examined. The used programs for thermochemical simulations were HSC Chemistry and Aspen Plus.

9.3.1 HSC Chemistry

Material and energy balances of the syngas and methanol cases were simulated with the HSC Chemistry program developed by Outotec Research Oy. HSC Chemistry is software used for chemical reaction and equilibrium calculations. The two calculation modules used in this study are the "Equilibrium Compositions" and "Heat and material Balances" modules. Equilibrium Compositions module enables to calculate multi-component equilibrium compositions in heterogeneous systems.

Heat and material balance module calculates the real or constrained heat balances with given mass balances as the boundary conditions, but not the theoretical balances at equilibrium conditions. (Outotec 2011)

9.3.2 Aspen Plus

Aspen Plus was used for the material and energy balance calculations in the DMC case. Aspen Plus is a process modelling environment that can be used in conceptual design, optimization, and performance monitoring for the chemical, polymer, specialty chemical, metals and minerals, and coal power industries. (Aspen Plus 2012)

9.3.3 Sustainability assessment questionnaire

Sustainability assessment was done using a questionnaire based on the twelve Green Chemistry principles shown in Table 13. The original questionnaire is based on the question lists made by Saavalainen et al. (2012) in the Mass and Heat Transfer Laboratory at the University of Oulu. It contains questions concerning the environmental, social and economic aspects of the processes. The questions are divided according to each of the principles of Green Chemistry.

10 Reforming (syngas production)

10.1 Material balances

The aim of the material balance calculations was to evaluate the effect of temperature and pressure on the product flow composition. The material balance of the reforming calculations was examined within the following components: CH_4, H_2O, CO_2, H_2, CO, C.

10.1.1 Material balances of SMR

The reaction for SMR is shown in Eq. (9):

$$CH_4 + H_2O \rightleftharpoons 3H_2 + CO \tag{9}$$

Reactants were fed in stoichiometric proportions. The effect of temperature was evaluated by calculating the equilibrium compositions in the range of 0 °C – 1000 °C and at 1 bar pressure. The temperature at which 95 % conversion of methane was reached was chosen as the reaction temperature. At this temperature the effect of pressure on the product compositions was evaluated by calculating the equilibrium compositions between pressure of 1 bar and pressure of 200 bar. Figure 26 represents the equilibrium concentrations in the methane steam reforming reaction between temperatures 0 °C and 1000 °C at 1 bar pressure.
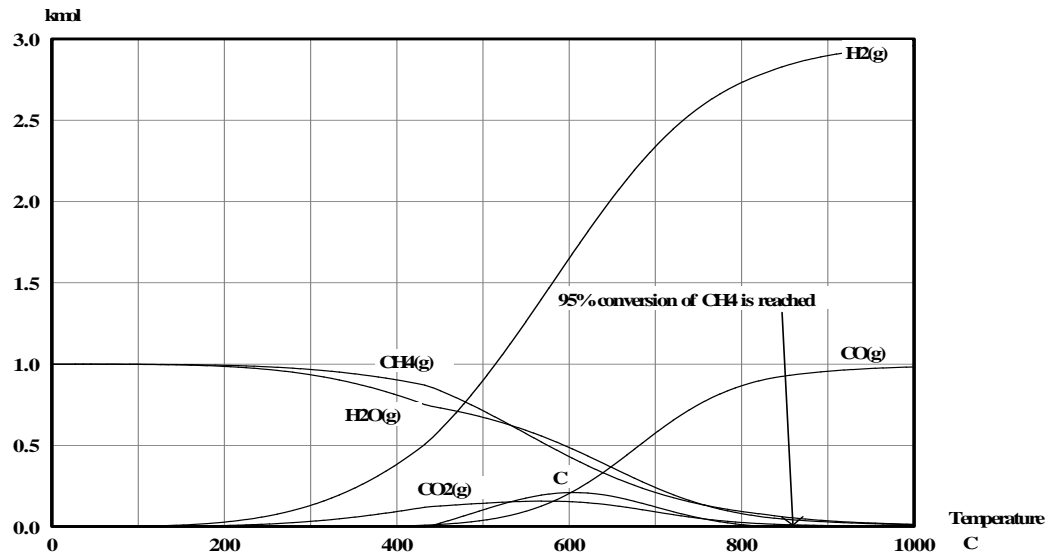
Figure 26. Effect of temperature on the equilibrium composition of SMR at atmospheric pressure with the temperature at which the 95 % conversion of methane is reached (marked with an arrow).

Figure 26 shows that the higher the temperature the higher the conversion of CH_4. The figure shows also that with 100 % conversion of raw materials syngas would be produced with a H_2/CO ratio of about 3 as the reaction equation shows. The 95 % conversion of methane was achieved at 869 °C. At this temperature no carbon is formed. The effect of pressure on the product concentration from 1 bar to 200 bar at 869 °C is depicted in Figure 27.
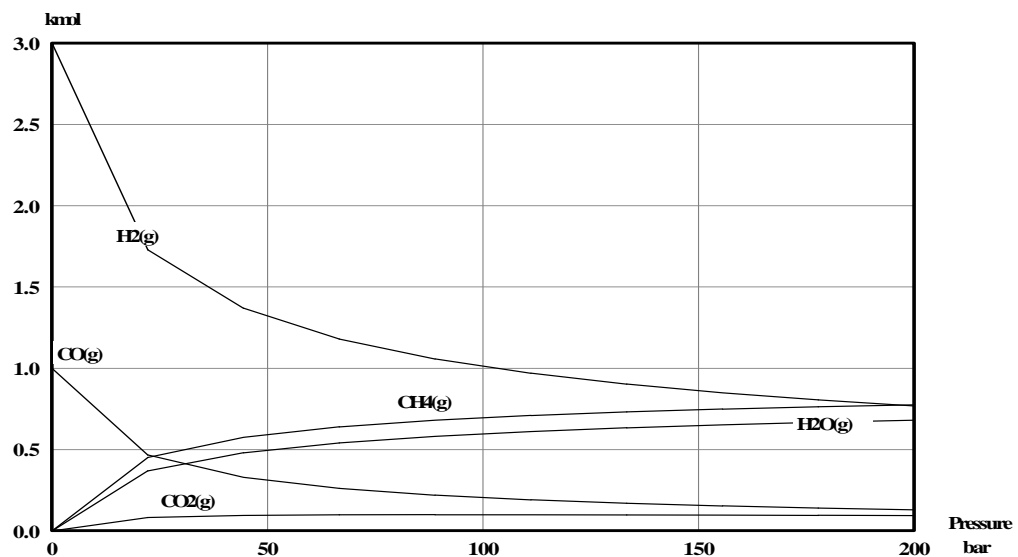
Figure 27. Effect of pressure on the equilibrium composition of SMR process at 869 °C.

As Figure 27 shows, increasing pressure does not increase the conversion of CH_4 or lead to higher syngas yield. Therefore atmospheric pressure is favourable and chosen as the simulation pressure.

10.1.2 Material balances of dry reforming

The dry reforming reaction is the following (11):

$$CH_4 + CO_2 \rightleftharpoons 2H_2 + 2CO \tag{11}$$

Reactants were fed in stoichiometric proportions. Operation temperature was selected at 95 % conversion of CH_4 was attained. At this temperature the effect of pressure on the product compositions was evaluated by calculating the equilibrium compositions between the pressure of 1 bar and the pressure of 200 bar. Figure 28 shows the equilibrium concentrations via the dry reforming reaction between temperatures 0 °C and 1000 °C and at 1 bar pressure.
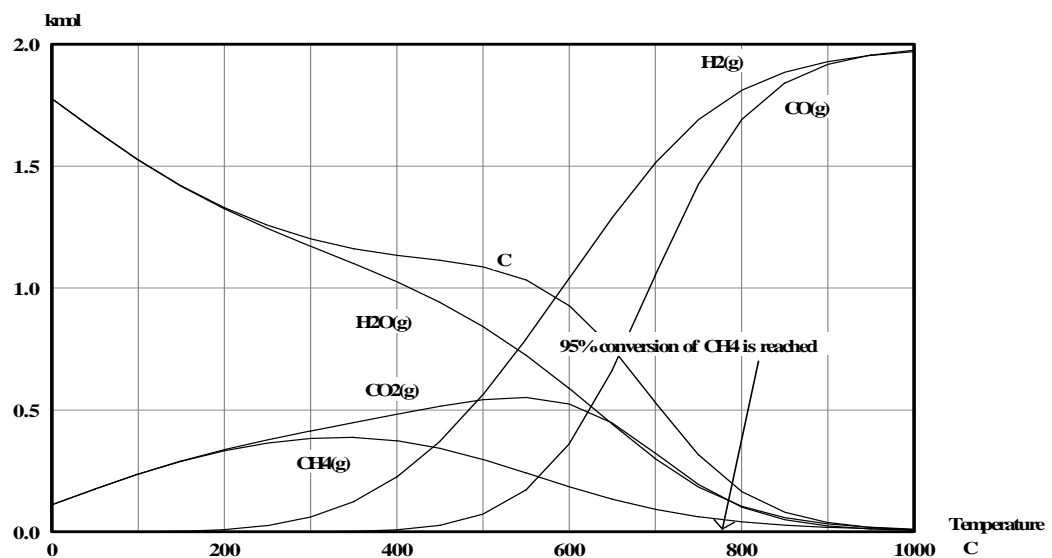
Figure 28. Effect of temperature on the equilibrium composition of dry reforming at atmospheric pressure with the temperature in which 95 % conversion of methane is reached (marked with an arrow).

As Figure 28 shows, the H_2/CO ratio is close to 1:1 at high temperatures. Low temperatures favour the formation of carbon. The 95 % conversion of CH_4 is achieved at temperature of 778 °C. Noteworthy is that at this temperature carbon is still produced. The effect of pressure on the product composition from 1 bar to 200 bar is shown in Figure 29.
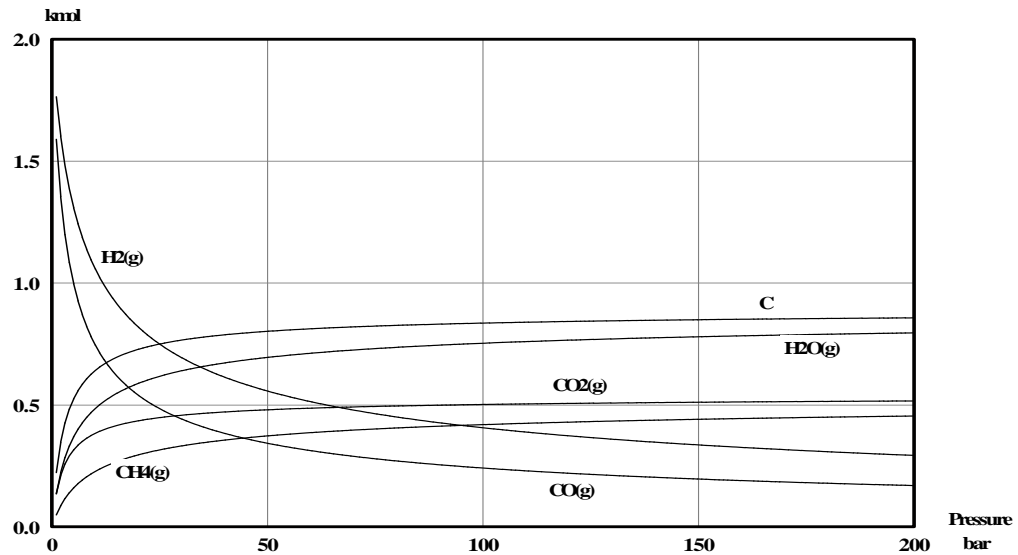
Figure 29. Effect of pressure on the equilibrium composition of dry reforming process at 778 °C.

Figure 29 shows that as in the SMR case, increasing pressure lowers the yield of syngas and gives a poorer conversion of CH_4. Therefore atmospheric pressure is favoured and chosen as the simulation pressure.

10.2 Energy balances

Feed and product concentrations were used to simulate the energy balance of each reaction. The energy balance simulation results indicated the amount of energy needed for the reaction to happen in certain process conditions. This reaction energy together with raw material processing energy was used to calculate the total energy needed for the process. The total energy consumption of a process was calculated as presented in Equation (26):

Total energy = Raw material processing energy + Reaction energy   (26)

Raw material processing energy includes all the feed flow compounds and the energy needed to produce them. CO_2 separation (in CO_2 utilizing routes) is calculated as a part of the raw material processing energy. End product separations were ignored.

The total energy consumption consists of reaction energy and raw material processing energy. The feed gas CH_4 amount is the same for both processes. Methane's heat value is 50.009 MJ/kg. 1 kmol of methane weights 16.043 kg. Therefore 1 kmol of methane has a heat value of 802.29 MJ. In SMR no raw material processing energy consumption is used because water as a raw material is assumed to be gotten without significant energy input. In reality some energy consumption comes from the water purification and pumping but the amount is very small compared to the process itself. CO_2 separation was assumed to be performed in an improved amine adsorption/stripping integrated plant the CO_2 removal efficiency being at 90 %. For every kmol of CO_2 recovered, 38.5 MJ of energy is needed (Halmann & Steinberg 1999, 137).

10.3 Material and energy balances

Table 15 shows the calculated material balances of the reforming cases.

Table 15. Material balances of the reforming cases.

Compound	SMR feed (kmol)	SMR product (kmol)	Dry feed (kmol)	Dry product (kmol)
H_2		0.753		0.526
CO		0.247		0.474
C				0.067
CH_4	0.263	0.013	0.298	0.015
H_2O	0.263	0.010		0.041
CO_2		0.003	0.298	0.041
Total syngas		1		1
Total co-products		0.026		0.164
Total products		1.026		1.164

As Table 15 shows, dry reforming process needs more methane to produce 1 kmol of syngas. The amount of co-products is also higher in the dry reforming case. There is also different syngas ratio for each process. For SMR syngas is produced

with a ratio of 3.05. For dry reforming the ratio is 1.11. Table 16 shows the energy balances of the two reforming cases.

Table 16. Energy consumptions of the reforming cases.

Process	SMR (MJ/syngas kmol)	Dry reforming (MJ/syngas kmol)
Raw materials	211.07	239.20
CO_2 separation		11.47
Reaction energy	77.82	87.11
Total energy	288.89	337.78

As Table 16 shows, due to the larger need of methane dry reforming has higher energy consumption of raw materials. Also reaction energy is slightly higher. Dry reforming energy consumption is 17 % higher compared to SMR energy consumption.

10.4 Economic analysis

The total costs of the processes (raw materials, raw material processing and reaction costs) were evaluated with different CO_2 taxes and CO_2 separation costs. The used CO_2 was assumed to be CO_2 for which the facility has to pay taxes if emitted into the atmosphere. Energy consumption was transferred to euro with the Nordpool 2010 price 0.0158 €/MJ (Savon Voima 2011).

Price of methane was assumed to be the price of natural gas. Amount of 35 €/MWh for small sized facility customers (Gasum Oy 2011) was used together with the heat value of methane to get the price of 7.80 €/kmol. The cost of producing 1 kmol of syngas with SMR and with dry reforming is shown in Figure 30 as a function of CO_2 tax.
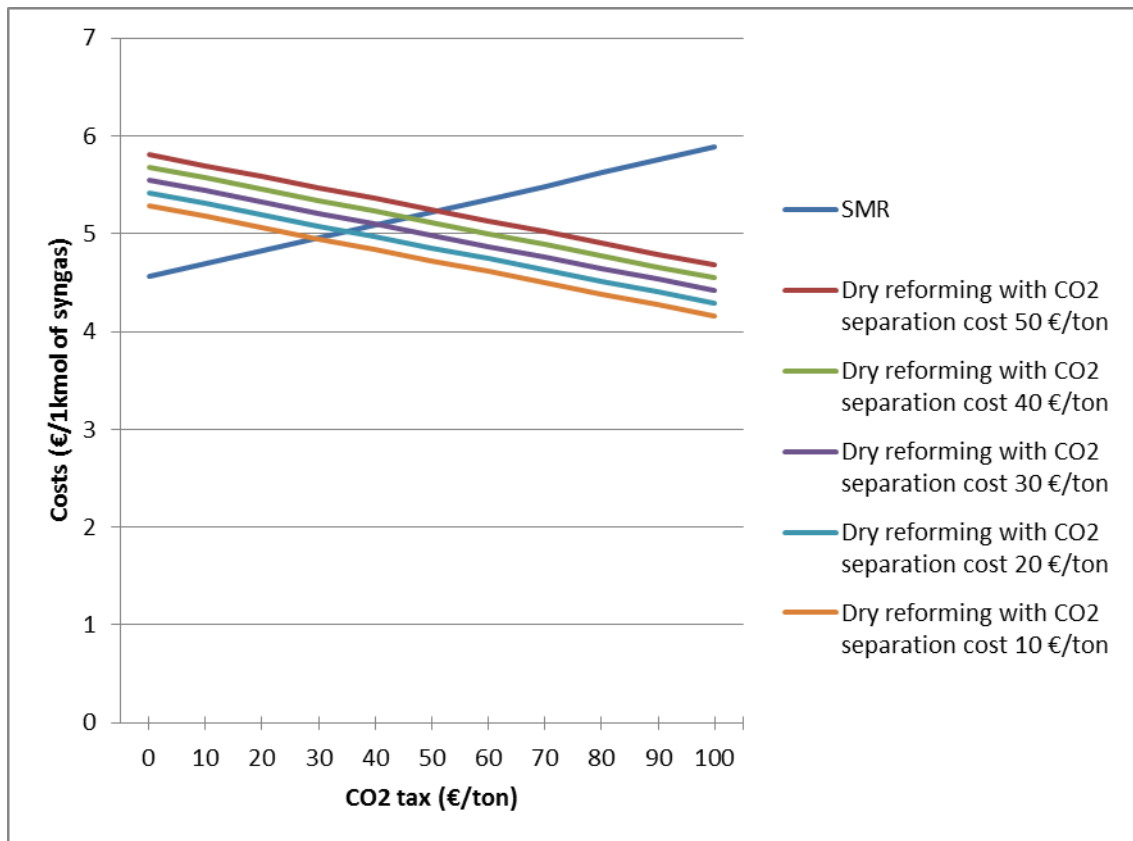
Figure 30. The cost of producing 1 kmol of syngas in the SMR and in the dry reforming with different separation costs as a function of CO_2 tax.

10.5 Sustainability assessment

Table 17 shows facts and assumptions made for the sustainability assessment.

Table 17. Facts and assumptions used in the sustainability assessment of SMR and dry reforming processes (CDC 2007, Dow 2011, Halmann & Steinberg 199, 317, KBR 2011).

Aspect	SMR	Dry reforming
Raw materials	CH_4 and H_2O.	CH_4 and CO_2 (from flue gas).
Main products	H_2 and CO with a ratio of 3.05 (Used in fuel production).	H_2 and CO with a ratio of 1.11 (Used in fuel production).
Side products	CH_4 and H_2O (recycled).	CH_4 and H_2O recycled, N_2 purged.
Wastes	0.003 kmol CO_2 for every produced syngas kmol.	0.041 kmol of unreacted CO_2 and 0.067 kmol of carbon for every produced syngas kmol.
Atom economy and yield	100 % atom economy. 3.801 kmol syngas/1 kmol fed methane yield.	100 % atom economy. 3.354 kmol syngas/1 kmol fed methane yield.
Process conditions	High temperature (869 °C) and low pressure (1 atm). Energy input of 289 MJ needed for every produced kmol of syngas.	Atmospheric pressure and high temperature (778 °C). Energy input of 337 MJ needed for every produced kmol of syngas.
Solvents and auxiliary chemicals	No solvents or auxiliary chemicals.	CO_2 separation uses an amine solvent MEA.
Plant specification	No gas leaks. CH_4 and H_2O sources on-site.	No gas leaks. CH_4 and CO_2 sources on-site.
Environmental issues	CH_4 and CO_2 are greenhouse gases.	
Safety issues	Similar safety issues concerning the high temperature and the flammable H_2, CH_4 and CO (also toxic). Dry reforming facility has additive safety issues concerning the MEA solvent and the high concentrated CO_2.	
Supply chain	Similar supply chains but additive logistics are needed in dry reforming facility because of the carbon side product and the MEA solvent.	
Alternative options	Alternative reaction: electrolysis (reaction conditions atmospheric but the process is more expensive). Alternative catalyst: Rh-catalyst.	
Catalysts	Ni-Al_2O_3.	

Sustainability assessment was conducted based on the assumptions and facts shown in Table 17. The sustainability assessment questionnaire and answers for the questions are shown in Appendix 1. Impacts were given the following points – positive impact +1 (green colour in the questionnaire), neutral impact 0 (yellow colour) and negative impact -1 (red colour). Total points in each principle were calculated. Table 18 shows the points in all of the 12 principles and summary points of all the principles.

Table 18. Sustainability points in each principle and total points for steam methane reforming and dry reforming processes.

Principle	SMR	Dry reforming
1st principle: Waste prevention	0	2
2nd principle: Atom economy optimization	5	2
3rd principle: Less hazardous syntheses	-2	1
4th principle: Safer chemicals and products	0	5
5th principle: Safer solvents and reaction conditions	2	-2
6th principle: Energy efficiency	-2	-2
7th principle: Renewable feedstock utilization	2	1
8th principle: Avoiding unnecessary derivization	8	8
9th principle: Catalyst usage	10	9
10th principle: Degradation of products	-2	1
11th principle: Process monitoring and analysis	2	0
12th principle: Minimizing the potential accidents	3	3
Total points	26	28

As shown in Table 18, dry reforming is the more sustainable process in the waste prevention principle because it consumes CO_2 rather than produces new CO_2 emissions. SMR on the other hand has better yield which is critical in the 2nd principle questions. The 3rd and 4th principle total points are affected by the negative points of SMR concerning the environmental issues. In safety issues the points of dry reforming are affected by its solvent use. This can be seen from the total points in the 5th principle. No clear difference in energy consumption was noted, which gives the same result in the 6th principle for both processes. The 7th principle includes a question about studies concerning the reactions. SMR is the more studied reaction which makes it to get one point more than the CO_2 utilizing process. There were no differences in derivization and potential accident minimization of principles 8 and 12. CO_2 does not degrade in dry reforming which is why dry reforming is more sustainable in the 10th principle. SMR has a long history as an industrial process while dry reforming is not used on industrial scale yet. This fact is the basis for the 0 points of dry reforming in the 11th principle questions. The difference in the 9th principle (catalyst usage) is relatively small although no industrial catalysts for dry reforming exist. In total points dry reforming has more points (28) compared to the SMR route (26 points).

11 Methanol synthesis

11.1 Material balances

The material balance of methanol synthesis was examined within the following components: CH_3OH, H_2O, CO_2, H_2 and CO.

11.1.1 Material balances of syngas route

The reaction for methanol synthesis via syngas route is shown in eq. (15):

$$2H_2 + CO \rightleftharpoons CH_3OH \tag{15}$$

Reactants were fed in stoichiometric proportions. The effect of temperature was evaluated by calculating the equilibrium compositions in the range of 25 °C - 1000 °C and at 1 bar pressure. Figure 31 represents the equilibrium concentrations in the methanol synthesis via syngas between temperatures 25 °C and 1000 °C at 1 bar pressure.
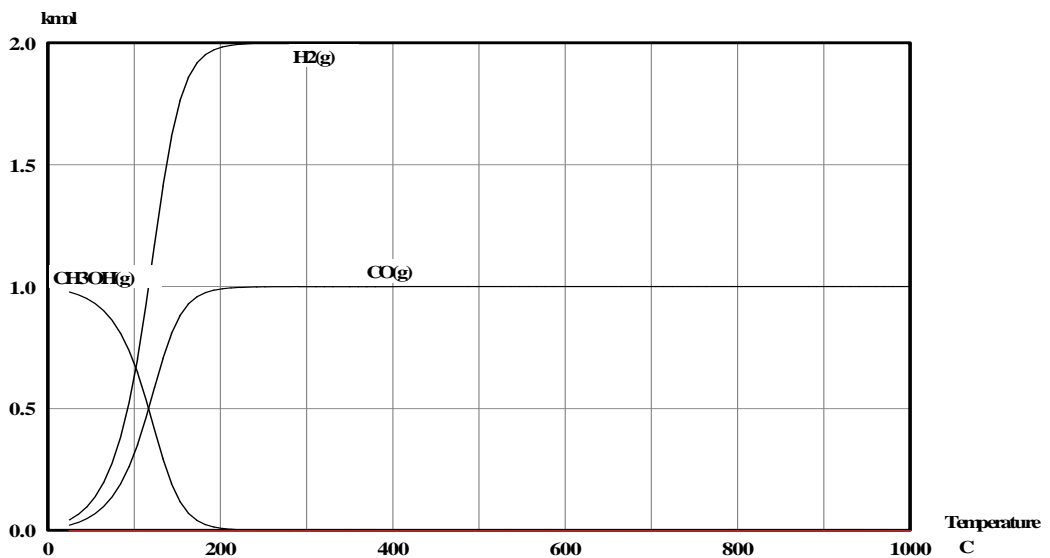
Figure 31. Effect of temperature on the equilibrium composition of methanol via syngas at 1 bar pressure.

Figure 31 shows that the lower the temperature, the higher the yield of methanol and the higher the conversion of raw materials. However, industrial methanol synthesis occurs at 180-300 °C because lower temperatures would lower the catalyst activity (Tijm et. al. 2001). Therefore methanol synthesis was simulated at 200 °C to correspond the industrial process conditions. The effect of pressure on the product concentrations from 1 bar to 200 bar (T= 200 °C) is depicted in Figure 32.
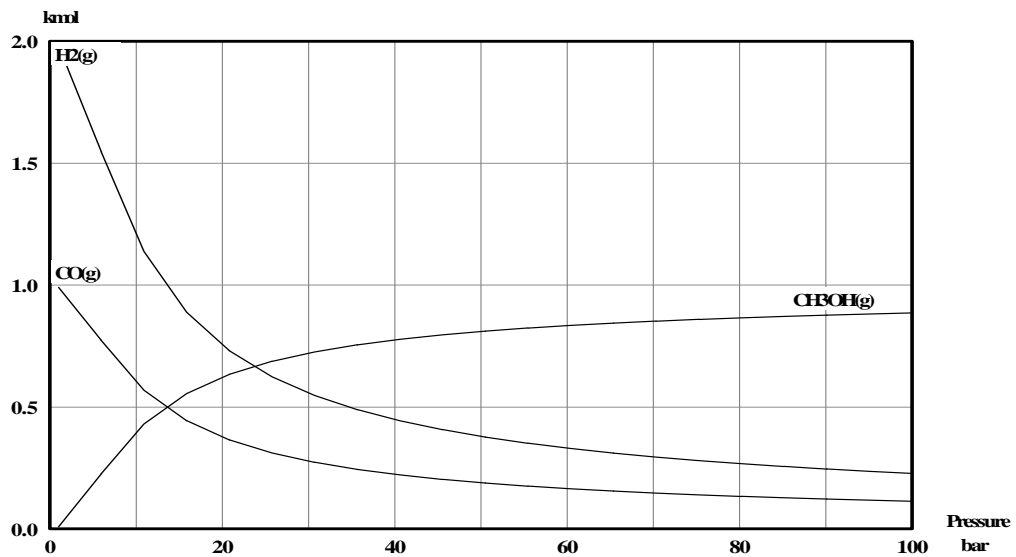
Figure 32. Effect of pressure on the equilibrium composition of methanol synthesis via syngas at 200 °C.

As Figure 32 shows, the pressure increase above 50 bar does not raise the yield of methanol very much. 50 bar pressure gives a good yield of methanol and does not need very high compression energy. Therefore it was chosen as the reaction pressure.

11.1.2 *Material balances of synthesis via CO$_2$*

Methanol synthesis via CO$_2$ was simulated with the following reaction: (16)

$$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O \qquad (16)$$

Reactants were fed in stoichiometric proportions. Figure 33 shows the equilibrium concentrations in methanol synthesis via CO_2 route between temperatures 25-1000 °C at atmospheric pressure.
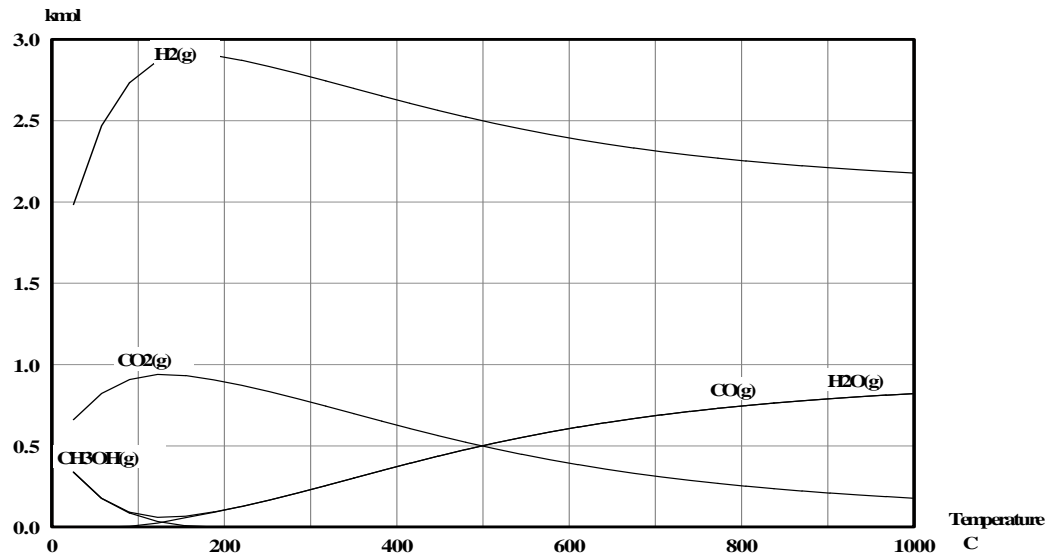
Figure 33. Effect of temperature on the equilibrium composition of methanol synthesis via CO_2 route at atmospheric pressure.

As Figure 33 shows, at 200 °C and atmospheric pressure no methanol is formed. According to Fiedler et al. (2012) the CO_2 reaction occurs with the same process conditions as the syngas route does. Therefore the same simulation temperature 200 °C can be used also for the CO_2 route. Figure 34 represents the equilibrium concentrations in methanol synthesis via CO_2 route between pressures 1 to 100 bar and at constant temperature of 200 °C.
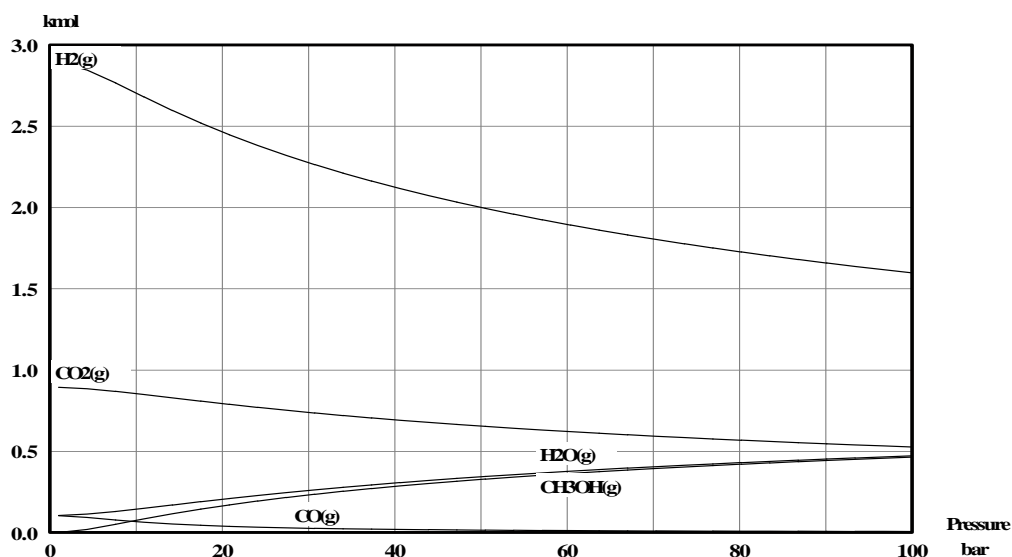
Figure 34. Effect of pressure on the equilibrium concentrations of methanol synthesis via CO_2 route at 200 °C.

As Figure 34 shows, methanol is formed at 200 °C when the pressure is raised from the atmospheric levels. At 50 bar the yield of methanol, however, is significantly lower than in the syngas route. This is mainly because the only product of syngas methanol synthesis is methanol, but CO_2 methanol synthesis produces as many moles of water as methanol.

11.2 Energy balances

The total energy consumption consists of reaction energy, energy of raw materials and raw material processing energy. Raw material energy consumption was calculated with the heat values of H_2 and CO. For CO this value is -282.96 MJ/kmol and for H_2 -241.83 MJ/kmol (HSC).

11.3 Material and energy balances

Table 19 shows the feed flow composition together with the product flow composition at 200 °C temperature and 50 bar pressure.

Table 19. Material balances of the methanol synthesis cases.

Compound	Syngas route feed (kmol)	Syngas route products (kmol)	CO_2 route feed (kmol)	CO_2 route products (kmol)
CH_3OH		1		1
H_2	2.469	0.469	9.146	6.101
H_2O		0		1.049
CO	1.235	0.235		0.049
CO_2		less than 10^{-5}	3.049	2
Total methanol		1		1
Total co-products		0.570		9.199
Total products		1.380		10.199

As Table 19 shows, the amount of by-products is significantly larger in the CO_2 based methanol synthesis. Also the amount of H_2 needed is more than three times larger in the CO_2 route. Table 20 shows the energy balances of the methanol synthesis cases.

Table 20. Energy consumptions of the methanol synthesis cases.

Process	Syngas route (MJ/methanol kmol)	CO_2 route (MJ/methanol kmol)
Raw materials	946.43	2211.83
CO_2 separation		117.38
Reaction energy	-90.44	-44.18
Total energy	855.99	2285.03

As seen from Table 20, there is a significant difference also in the energy consumptions of the two routes. The amount of energy consumption in the syngas based methanol synthesis is only 37 % of the total energy consumption of the CO_2 route.

11.4 Economic analysis

The total costs of the processes (raw materials, raw material processing and reaction costs) were evaluated with different CO_2 taxes and CO_2 separation costs. The used CO_2 was assumed to be CO_2 for which the facility has to pay taxes if emitted into the atmosphere. Energy consumption was transferred to euros with the Nordpool 2010 price 0.0158 €/MJ (Savon Voima 2011). Reaction heat was assumed to be utilized in the process. H_2 and CO prices were calculated from their heat values. (4.47 €/kmol for H_2 and 3.82 €/kmol for CO). The cost of producing 1 kmol of

methanol via syngas route and via CO_2 route is shown in Figure 35 as a function of CO_2 tax.
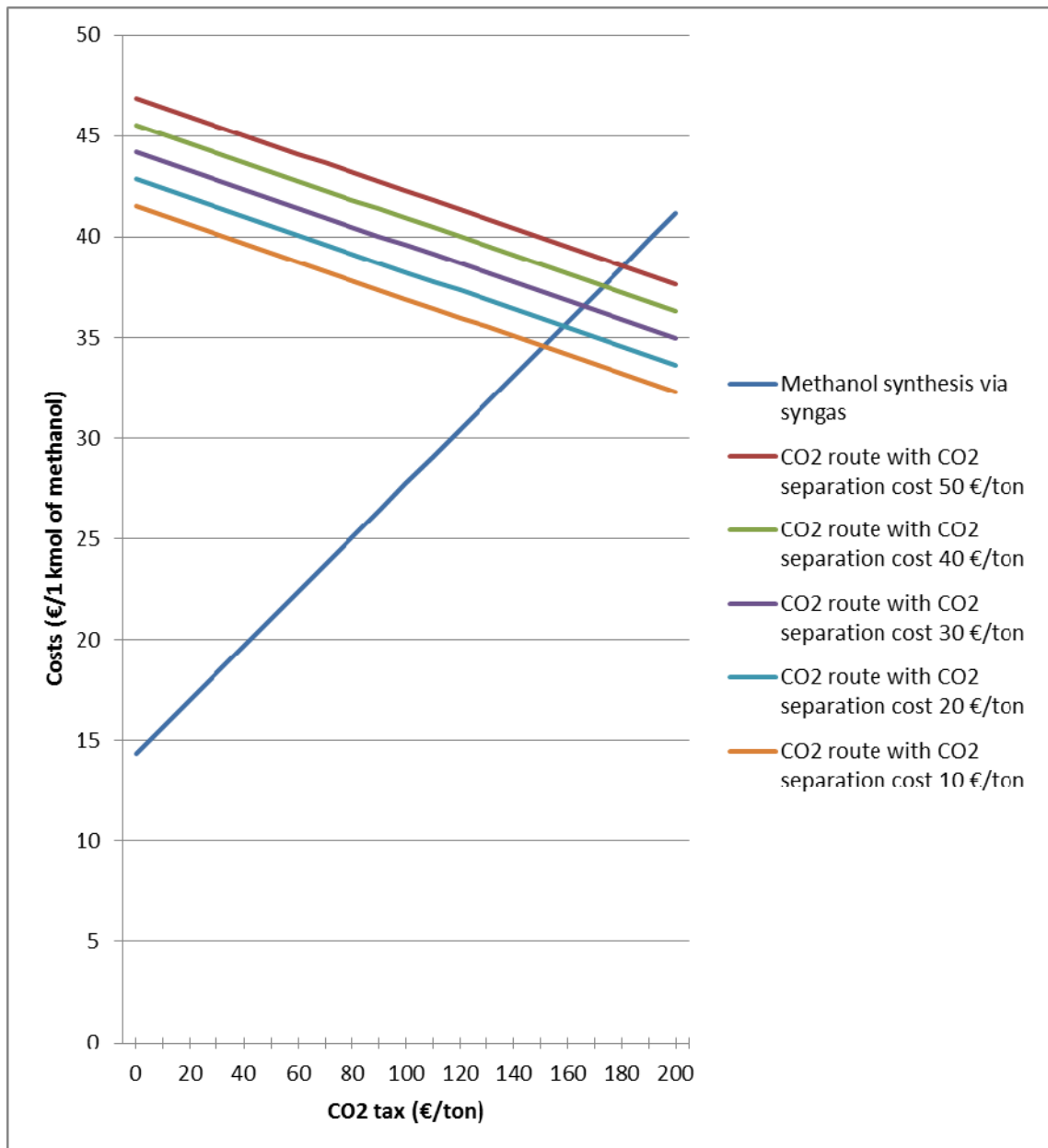
Figure 35. The cost of producing 1 kmol of methanol in the syngas route and in the CO_2 route with different separation costs as a function of CO_2 tax.

As seen from Figure 35, the CO_2 route is about three times as expensive as syngas route at low CO_2 tax costs.

11.5 Sustainability assessment

Table 21 shows facts and assumptions made for the sustainability assessment.

Table 21. Facts and assumptions used in the sustainability assessment of methanol synthesis via syngas vs. methanol synthesis via CO_2 (Fiedler et al. 1990, 478 & Tijm et al. 2001, KBR 2011).

Aspect	Syngas route	CO_2 route
Raw materials	H_2 and CO. Syngas is from a syngas facility on-site.	H_2 and CO_2 (from flue gas). H_2 is pumped from a syngas facility on-site.
Main products	Methanol (used in another chemical synthesis).	Methanol (used in another chemical synthesis).
Side products	H_2 and CO (recycled).	N_2 and CO_2 purged, H_2 recycled and CO and H_2O utilized as energy.
Wastes	No wastes.	Unreacted CO_2.
Atom economy and yield	100 % atom economy. 0.405 kmol methanol/1 kmol fed hydrogen yield.	64.0 % atom economy. 0.109 kmol methanol/1 kmol fed hydrogen yield.
Solvents and auxiliary chemicals	No solvents or auxiliary chemicals.	CO_2 separation uses an amine solvent MEA.
Plant specification	No leaks. Syngas source on-site.	No gas leaks. Hydrogen source on-site.
Environmental issues	CO_2 is a greenhouse gas.	
Safety issues	Similar safety issues concerning the flammable H_2 and CO (also toxic). CO_2 route has additive safety issues concerning the MEA solvent and high concentrated CO_2.	
Supply chain	Similar supply chains.	
Alternative options	Alternative catalyst: noble metal catalyst (not economically feasible).	
Catalysts	$Cu/ZnO/Al_2O_3$.	
Process conditions	Lean conditions (200 °C and 50 bar).	

The sustainability assessment questionnaire and answers for the questions is shown in Appendix 2. Impacts were given the following points: positive impact +1, neutral impact 0 and negative impact -1. Total points in each principle were calculated. Table 22 shows the points in all of the 12 principles and summary points of all the principles.

Table 22. Sustainability points in each principle and total points for methanol synthesis via syngas and methanol synthesis via CO_2.

Principle	Syngas	CO_2
1st principle: Waste prevention	8	8
2nd principle: Atom economy optimization	5	-2
3rd principle: Less hazardous syntheses	5	6
4th principle: Safer chemicals and products	4	6
5th principle: Safer solvents and reaction conditions	3	0
6th principle: Energy efficiency	3	3
7th principle: Renewable feedstock utilization	3	2
8th principle: Avoiding unnecessary derivization	8	8
9th principle: Catalyst usage	13	13
10th principle: Degradation of products	1	1
11th principle: Process monitoring and analysis	2	2
12th principle: Minimizing the potential accidents	4	4
Total points	59	51

As summarized in Table 22, there are no differences in the waste prevention principle. This is mainly because of the lack of wastes in both processes. The syngas route is the better process in the 2nd principle because of its better atom economy and yield of methanol. The CO_2 route is a slightly better process in the 3rd and 4th principle because of the lack of the hazardous CO as a raw material. However, the solvent use of the CO_2 capture makes its points in the 5th principle lower compared to the syngas route. There were no differences in the energy efficiency of the 6th principle, derivization of the 8th principle, catalyst usage of the 9th principle, product degradation of the 10th principle, process monitoring of the 11th principle and potential accident minimization of the 12th principle. The more studied reaction route of the syngas process gives it better points in the 7th principle. In total points the syngas route has 59 points compared to the 51 points of the CO_2 route.

12 DMC production

In the DMC production the post-70's oxidative carbonylation route and the direct synthesis of DMC via CO_2 route were compared. DMC routes were simulated with Aspen Plus as no thermodynamic data for DMC was found from HSC Chemistry.

12.1 Material balances

The material balances of the DMC cases were calculated with the following components: CH_3OH, H_2O, CO_2 and CO.

The reaction for the oxidative carbonylation route is shown in eq. (26):

$$2CH_3OH + CO + 1/2O_2 \rightleftharpoons C_3H_6O_3 + H_2O \tag{26}$$
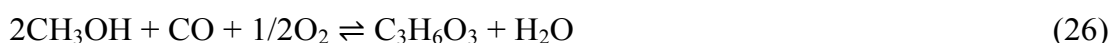
The case reaction for the DMC synthesis via the CO_2 route is shown in Equation (27):
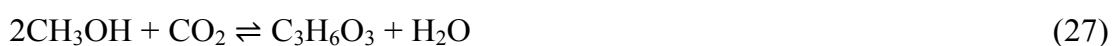
$$2CH_3OH + CO_2 \rightleftharpoons C_3H_6O_3 + H_2O \tag{27}$$

Reactants were fed in stoichiometric proportions. The effect of temperature was evaluated by calculating the equilibrium composition in the range of 0–200 °C and at atmospheric pressure. On the contrary to the syngas and methanol cases, in the DMC case in the material balances only the amount of DMC is shown as a graph.
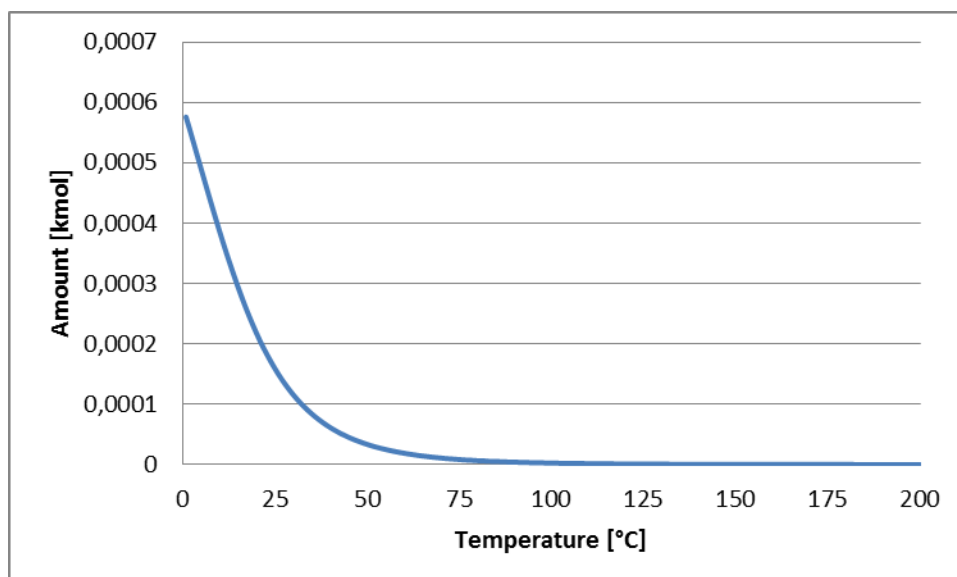
Figure 36. Effect of temperature on the DMC yield at 0–200 °C and at atmospheric pressure.

As Figure 36 shows, the lower the temperature, the higher the DMC yield. It is also seen that the DMC yield drops to zero near the temperature of 100 °C. Industrial processes of oxidative carbonylation occur at temperatures of about 100 °C (Pachecho & Marshall 1997). Therefore 100 °C is chosen as the temperature in the DMC cases. Figure 37 shows the effect of pressure on the DMC yield at 100 °C.
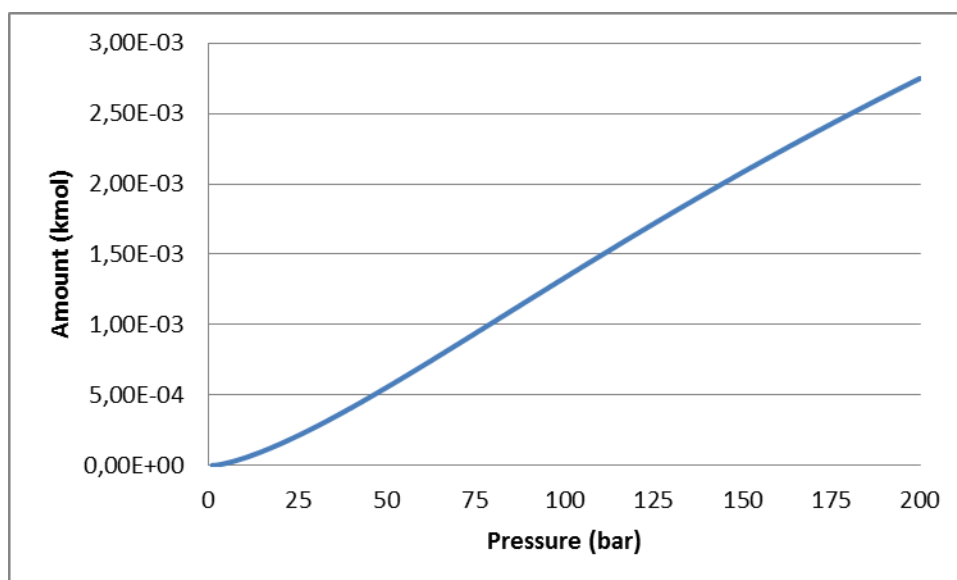
Figure 37. Effect of pressure on the DMC yield at 100 °C.

As Figure 37 shows, DMC yield rises linearly as pressure rises. Pressure of 100 bar is chosen as the pressure in the DMC cases.

12.2 Energy balances

The total energy consumption consists of reaction energy, energy of raw materials and raw material processing energy. Raw material energy consumption was calculated with the heat values. For methanol the heat value is -338 MJ/kmol and for CO -282.96 MJ/kmol. Energy consumption in O_2 production was assumed 2.88 MJ/kmol according to Stålhandske (2009). CO_2 separations were assumed to be performed in an improved amine adsorption / stripping integrated facility. Every kmol of CO_2 recovered thus needs an energy input of 38.5 MJ (Halmann & Steinberg 1999, 137).

12.3 Material and energy balances

Table 23 shows the product composition obtained at the temperature of 100 °C and pressure of 100 bar.

Table 23. Material balances of the DMC cases.

Compound	Oxy route feed (kmol)	Oxy route product (kmol)	CO_2 route feed (kmol)	CO_2 route products (kmol)
CO	1000	6		6
CO_2		994	1000	994
H_2O		6		6
CH_3OH	2000	1995	2000	1995
O_2	500			
DMC		1		1
Total DMC		1		1
Total co-products		3001		3001
Total products		3002		3002

As seen from Table 23, the DMC yield is very low compared to the yield of other products (yield 0.14-% based on fed MeOH). All of the O_2 fed in oxidative carbonylation is consumed. New anthropogenic CO_2 emissions are produced a lot in the carbonylation case. In the CO_2 case 0.6-% of CO_2 fed is consumed. The energy consumptions of the two processes are shown in Table 24.

Table 24. Energy consumptions of the DMC cases.

Process	Carbonylation (MJ/DMC kmol)	CO_2 route (MJ/DMC kmol)
Raw materials	1100440	676000
Processing of raw materials	0	38500
Energy consumption of the reaction	−208620	78500
Total energy consumption	891820	793000

Calculated from the information in Table 24, the total energy consumption of the CO_2 route is 88.9% from the energy consumption of the carbonylation route.

12.4 Economic analysis

The total costs of the processes (raw materials, raw material processing and reaction costs) were evaluated with different CO_2 taxes and CO_2 separation costs. The used CO_2 was assumed to be CO_2 for which the facility has to pay taxes if emitted into the atmosphere. Energy consumption was transferred to euros with the Nordpool 2010 price 0.0158 €/MJ (Savon Voima 2011). Reaction heat was assumed to be utilized in the process. H_2 and CO prices were calculated from their heat values. (4.47 €/kmol for H_2 and 3.82 €/kmol for CO). The cost of producing 1 kmol of DMC via carbonylation route and via CO_2 route is shown in Figure 38 as a function of CO_2 tax. Methanol, and CO prices were calculated from heat values. This gave the prices 5.34 €/kmol for methanol and 3.82 €/kmol for CO. O_2 price was found to be 45 €/ton, which is 1.44 €/kmol (Korhonen 2010).
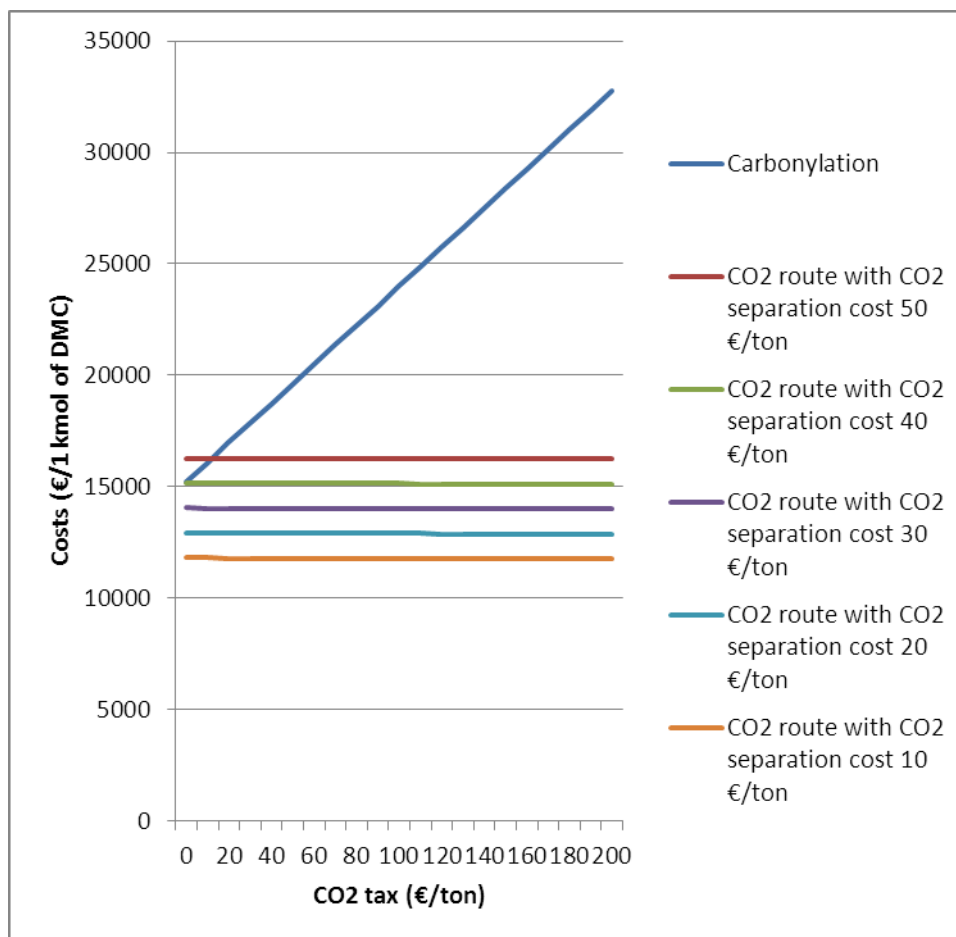
Figure 38. The cost of producing 1 kmol of DMC with carbonylation route and with CO_2 route as a function of CO_2 tax cost.

As Figure 38 shows, carbonylation route costs quickly rise when the CO_2 tax cost rises. The CO_2 route is close to being a competitive process at the current CO_2 tax prices (less than 10 €) if the CO_2 separation could be done at 40 €/ton or less (future estimation).

12.5 Sustainability assessment

Table 25 shows the facts and assumptions used for the sustainability assessment questionnaire.

Table 25. Facts and assumptions used in the DMC sustainability assessment.

Aspect	Oxydative carbonylation	CO_2 route
Raw materials	CH_3OH, CO and O_2.	CH_3OH and CO_2.
Side products	CO and CH_3OH recycled, H_2O and CO_2 purged.	N_2 purged, CO, CH_3OH and H_2O recycled.
Wastes	CO_2.	Basically no CO_2 is consumed.
Atom economy and yield	89.4 % atom economy. 0.001 kmol DMC / 2 kmol fed methanol	83.3 % atom economy. 0.001 kmol DMC / 2 kmol fed methanol
Catalysts	Copper oxide and zinc oxide on a carrier of aluminium oxide.	ZrO_2+CeO_2.
Solvents and auxiliary chemicals	No solvents or auxiliary chemicals.	CO_2 separation uses an amine solvent MEA. MEA based absorption is the cheapest process for CO_2 separation.
Main product	DMC - used in chemical syntheses.	
Process conditions	High pressure (100 bar) and mild temperature (100 °C).	
Plant specification	No gas leaks. The raw materials are pumped at 100 % concentrations on-site.	
Environmental issues	Both H_2 and CO are flammable.	
Safety issues	CO is toxic for human.	
Supply chain	Similar supply chains.	
Alternative options	Phosgenation as the alternative process. Phosgene route has better yield and operates at atmospheric conditions but has many environmental issues.	

Sustainability assessment was conducted based on the assumptions and facts shown in Table 25. The sustainability assessment questionnaire and answers for the questions are shown in Appendix 3. Total points in each principle were calculated. Table 26 shows the points in all of the 12 principles and summary points of all the principles.

Table 26. Sustainability points of the two processes.

Category of sustainability points	Carbonylation	CO_2
1st principle: Waste prevention	- 1	7
2nd principle: Atom economy optimization	- 2	- 3
3rd principle: Less hazardous syntheses	3	7
4th principle: Safer chemicals and products	1	5
5th principle: Safer solvents and reaction conditions	2	0
6th principle: Energy efficiency	7	7
7th principle: Renewable feedstock utilization	5	3
8th principle: Avoiding unnecessary derivization	6	6
9th principle: Catalyst usage	12	12
10th principle: Degradation of products	2	4
11th principle: Process monitoring and analysis	4	4
12th principle: Minimizing the potential accidents	6	6
Total points	45	59

As seen from Table 26, the CO_2 route has more points than carbonylation route in the first principle. Basically this is because of the large amount of new anthropogenic CO_2 emissions in the carbonylation route. Atom economy is slightly better in the carbonylation route which gives it better points in the second principle. The CO_2 route is the safer process option as seen from principles three and four mainly because of the lack of CO in the raw materials and lack of new anthropogenic CO_2 emissions. Carbonylation route needs no solvents which results in higher points in the 5th principle. Carbonylation route produces new CO_2 emissions that do not degrade, which is the reason for the lower points in the 10th principle. Although the carbonylation reaction produces energy and the CO_2 reaction consumes energy, there is no difference of points in the 6th principle. There is more experience of carbonylation route in industrial processes which gives it better points in the 7th principle. No difference was found in the derivization questions (principle 8), catalyst usage (principle 9), process monitoring (principle 11) or potential accident minimization (principle 12). In total points the CO_2 route has more points (59 points compared to the 45 points of the carbonylation route).

13 Summary of results and discussion

13.1 Reforming

The reforming case results are summarized in Table 27.

Table 27. Summary of reforming cases.

	Steam methane reforming	Dry reforming
Yield of syngas (based on feed)	3.801 kmol syngas / 1 kmol fed methane	3.354 kmol syngas / 1 kmol fed methane
Amount of wastes per 1 kmol of produced syngas	0.003 kmol CO_2.	0.041 kmol CO_2 (0.257 kmol used) and 0.067 kmol carbon.
Energy consumption per 1 kmol of produced syngas	289 MJ	337 MJ
Syngas production cost with 20 €/ton separation costs and 10 €/ton CO_2 tax (Figure 30)	0.60 €/kg	0.34 €/kg
Total sustainability points	26	28
Environmental points	10	13
Social points	11	13
Economic points	7	3

As seen from Table 27, SMR has higher yield of syngas based on fed methane. SMR produces a small amount of new anthropogenic CO_2 emissions. Dry reforming consumes a lot of CO_2 (0.257 kmol for every produced syngas kmol) but produces carbon as a side product (waste that deactivates catalyst). Energy consumption is higher in dry reforming case. Syngas production cost in kg is lower in dry reforming case as it produces the heavier but not as valuable CO a lot.

Environmental points include questions that have two categories (environmental/social or environmental/economical etc.). Therefore the sum of the three category points is not the same as the total. Dry reforming is slightly better than SMR in total sustainability points. SMR gets better points than dry reforming in the economic questions of sustainability assessment. Environmentally and socially dry reforming is the better option.

If the future legislation makes it even easier for CO_2 consuming processes to have economic advantage, dry reforming has the potential to become a serious competing process in the syngas production markets. Also if CO demand is raised, the low

H$_2$/CO ratio syngas producing dry reforming route could become more interesting for markets. Possible future implementations of large scale Fischer-Tropsch synthesis facilities for example might provide the need for more CO production in the world (FT-process uses a low H$_2$/CO ratio syngas).

The problem of dry reforming is the carbon formation. Formed carbon easily covers the active sites of catalyst particles and therefore the catalyst ceases to hasten the reaction (de Oliveira-Vigier et al. 2005). This is the main reason why there is no commercial processes using dry reforming process at the moment. Catalyst research is still needed in order to find carbon resistant catalysts. Because of the catalyst problems SMR is the preferred industrial process. It is not as sustainable as dry reforming but it performs better on commercial scale and is economically the better process at the CO$_2$ tax level of today (less than 10 €/ton). If the catalyst deactivation problems can be avoided with further research and if low H$_2$/CO proportion suffices, dry reforming has the potential to be a large scale industrial process.

13.2 Methanol synthesis

The methanol synthesis case results are summarized in Table 28.

Table 28. Summary of methanol synthesis cases.

	Syngas route	CO$_2$ route
Yield of methanol (based on feed)	0.405 kmol methanol / 1 kmol fed hydrogen	0.109 kmol methanol / 1 kmol fed hydrogen
Amount of wastes per 1 kmol of produced methanol	No wastes.	2 kmol CO$_2$ (1.049 kmol used)
Energy consumption per 1 kmol of produced methanol	856 MJ	2285 MJ
Methanol production cost with 20 €/ton separation costs and 10 €/ton CO$_2$ tax (Figure 35)	0.47 €/kg	1.34 €/kg
Total sustainability points	59	51
Environmental points	31	28
Social points	15	15
Economic points	17	11

As Table 28 shows, the syngas route is a lot better process in terms of yield. The CO$_2$ route consumes a rather high amount of CO$_2$ 33.67 % of all fed CO$_2$ while

producing valuable methanol. Energy consumption is nearly 3 times higher in the CO_2 route. The syngas route is commercially cheaper process with the selected CO_2 tax and separation costs. The syngas route has also more sustainability points. Social aspects are at the same level but in environmental and economic categories the methanol via syngas route performs better.

CO_2 is used already in industrial methanol synthesis as one of the feedstocks. Researchers still argue, how big proportion of the synthesized methanol is from the CO_2 reaction. Some have even claimed that all of formed methanol comes from the CO_2 reaction. The fact that the process is already used on industrial scale makes it a probable utilization chemical for a large scale CO_2 capture facility and an interesting route to research. However, catalyst and process optimization research is still needed before CO_2 route using methanol synthesis can be processed in a commercial facility. The price of 0.47 €/kg in the syngas route is high compared to the value of 0.30 €/kg found. (NG-tech 2012)

13.3 DMC production

The DMC production case results are summarized in Table 29.

Table 29. Summary of DMC cases.

	Oxidative carbonylation	CO_2 route
Yield of DMC (based on feed)	0.001 kmol DMC / 2 kmol fed methanol	0.001 kmol DMC / 2 kmol fed methanol
Amount of wastes per 1 kmol of produced DMC	994 kmol CO_2	994 kmol CO_2 (6 kmol used)
Energy consumption per 1 kmol of produced DMC	891820 MJ	793000 MJ
DMC production cost with 20 €/ton separation costs and 10 €/ton CO_2 tax (Figure 38)	1776 €/kg	1388 €/kg
Total sustainability points	45	58
Environmental points	25	33
Social points	10	12
Economic points	7	11

As Table 29 shows, carbonylation is the more expensive process to produce DMC. This is mainly because it creates new anthropogenic CO_2 emissions and has higher energy consumption.

According to the sustainability assessment, CO_2 has a clear advantage over the carbonylation route. CO_2 route is the more sustainable process especially concerning the environmental aspects. This is mostly because of the anthropogenic CO_2 emissions of carbonylation route. Also the lack of CO as raw material in the CO_2 process gives social and environmental advantage. Industrially working synthesis of DMC via CO_2 is on the research level. The need for a drying agent together with a catalyst makes it difficult to commercialize the process.

13.4 Discussion

There are some speculative issues concerning this research. For example no separation of CO_2 from the end product was assumed to take place. It was also assumed that the used CO_2 is excessive CO_2 that the facility has to pay taxes if it is not consumed. Also assumed was that taxes are paid for the unreacted CO_2 left from the reaction equilibrium.

Chemical utilization of CO_2 was found to be a promising way to use CO_2 if a capture facility is built. It was pointed out that further research should concentrate on finding more exact information with the help of laboratory tests and more extensive simulations for a case research. Feasibility studies such as this study are needed in order to evaluate the overall economics and sustainability of chemical utilization of CO_2.

From the three selected CO_2 routes (dry reforming, methanol synthesis via CO_2 and direct synthesis of DMC via CO_2) dry reforming consumes most of the fed CO_2 (86.3-% of all the CO_2 fed compared to 33.67 % of methanol and less than 0.001% of DMC).

As this research proofed, atom economy has not very much anything to do with real life processes. The newer green chemistry metrics, such as reaction mass efficiency

could substitute atom economy. On the other hand, the questionnaire includes atom economy together with yield, which is not a theoretically calculated metric. Still, for example in the reforming case SMR and dry reforming had the same colours and points in the atom economy questions although SMR clearly had the better yield of syngas and less side products.

The sustainability assessment questionnaire used was found as a great potential tool to evaluate and compare processes at the stage of conceptual process development. Assumptions had to be made in order to answer the complete questionnaire. Further research is needed in order to get additive results from computer simulations and laboratory tests before conducting a more precise sustainability assessment for the selected routes. Answering the sustainability assessment questions neutrally enough was found rather difficult despite precise information from simulations, laboratory tests and literature reviews. The feasibility of the sustainability assessment questionnaire should therefore be developed so that answering is simple and easy for anyone using the tool. Noteworthy is also that for example in the catalyst questions of DMC case no difference was found although the catalysts are different.

14 Conclusion

The main purpose of this thesis was to evaluate the feasibility and sustainability of the selected CO_2 utilizing reaction routes. In the literature the chemical properties, sources and legislation of CO_2 was reviewed along with CO_2 capture methods concentrating on post-combustion capture. Industrial applications of CO_2 utilization used today were summarized. Three selected conventional route vs. CO_2 utilizing route pairs were reviewed. These routes were syngas production via steam methane reforming (SMR) vs. dry reforming, methanol synthesis vs. methanol synthesis via CO_2 and dimethylcarbonate (DMC) production via oxidative carbonylation vs. direct synthesis of DMC via CO_2. The process technology of each route was reviewed concentrating on reactors and catalysts. Also further developments in the reactor and catalyst sectors were included. Literature part ended with a review of sustainability assessment as a tool for engineers.

The aim of the empirical part was to do a feasibility study and a sustainability assessment for the selected CO_2 utilizing reaction routes. The results were used to compare the conventional process and the CO_2 utilizing process. Feasibility study of each route consisted of thermodynamic study and economic study. Thermodynamic calculations were done with HSC Chemistry (syngas and methanol cases) and Aspen Plus (DMC case). The material and energy balances gotten from thermodynamic studies were the basis for economic studies. Different CO_2 tax costs and CO_2 separation costs were used to evaluate the costs of the conventional process and the CO_2 utilizing process. Facts and assumptions of each process were gathered to be used in the sustainability assessment questionnaire. The questionnaire based on 12 principles of Green Chemistry consists of questions concerning the environmental, social and economical impacts of the processes.

Facts and assumptions made based on the literature review and the thermodynamic and economic calculations were used when answering the sustainability assessment questionnaire. Results of each case study were summarized and discussed together with a discussion of the whole work.

Dry reforming was found slightly more sustainable process to produce synthesis gas but SMR performed better in the feasibility study and in the economic questions of

the sustainability assessment. Dry reforming is not a commercial process yet but has potential in the future if the problems in catalyst deactivation via carbon formation can be suppressed and there is a need for gas streams with low H_2/CO ratios. Before that the economically well performing and lots of hydrogen producing methane steam reforming is preferred commercially compared to the dry reforming reaction.

Methanol synthesis via syngas performed better in both the feasibility and the sustainability study. Still, methanol has the greatest short term potential for larger scale chemical utilization of CO_2 as the CO_2 utilizing reaction is already used together with the syngas reaction in real life facilities.

The DMC production via oxidative carbonylation was more expensive than the CO_2 utilizing DMC synthesis. Also in the sustainability assessment the CO_2 route was the better process. Mostly this was because of the environmental issues with carbonylation route (anthropogenic CO_2 emissions, CO use etc.). Direct synthesis of DMC via CO_2 still requires intensive research.

Chemical utilization of CO_2 was found to be a promising way to use CO_2 if a capture facility is built. This research used a lot of assumptions to evaluate the feasibility and sustainability of the selected routes. It was pointed out that further research should concentrate on finding more exact information with the help of laboratory tests and more extensive simulations for a case research.

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Question	SMR	DRY	Explanation
Green Chemistry Principle 1			*Waste prevention*
Environmental			
Does the process produce waste?	red	yellow	SMR produces CO_2, DRY coke.
Could this waste be utilised somewhere?	yellow	red	Yes (SMR) but not cost-effectively.
Is the waste hazardous?	yellow	green	CO_2 hazardous to environment.
Are there viable process modifications that would produce less waste?	green	green	Yes, higher temperatures lower the amount of wastes.
Have you considered the amounts of waste produced in the supply chain of the raw materials for your process?	green	green	Similar supply chains.
Have you considered the routes of product/by-product and wastes from the production through the end-of-life?	yellow	yellow	Syngas burns into CO_2 after use.
Social			
Are there any health and safety issues related to the harmful nature of waste?	green	green	No, CO_2 and C are harmless as concentrations are relatively low.
Economic			
Could there be significant cost related to the treatment and disposal of the waste?	red	yellow	Yes, CO_2 tax costs. Carbon disposal not very expensive.
Can the waste be used as a valuable side-product?	red	red	CO_2 of SMR and C of DRM are not cost-effectively utilizable.
Green Chemistry Principle 2			*Atom economy optimization*
Environmental/Social			
Have you calculated the atom economy for all possible reaction routes and selected the best one?	green	green	100 % atom economy in both cases.
Does your synthetic process have high yield?	green	yellow	SMR slightly higher.
Are there better alternative synthetic routes that could be used in process or reaction in terms of yield?	red	red	Yes, electrolysis.
Social			
Could the alternative reaction route improve the safety of the reaction conditions?	red	red	Yes, electrolysis works at atmospheric temperatures.
Are the health impacts minimized?	green	green	Yes.
Economic			
Could the use of this alternative route reduce the production cost?	green	green	Electrolysis is more expensive.
Do all the materials entering the process come out as part of saleable product?	green	yellow	No, but the amount of side products small in SMR.
Have you calculated the atom economy for all possible reactions routes and selected the best one?	green	green	Both reactions have an atom economy of 100 %.
Does your synthetic process have high yield?	green	yellow	SMR slightly higher.

Green Chemistry Principle 3			Less hazardous syntheses
Environmental			
Does your reaction use or generate materials that are potentially harmful?	red	yellow	CO_2 is used in dry reforming. In SMR it is produced.
Are the chemicals used registered within REACH?	green	green	Yes.
Could there be alternative processes that would use or generate less harmful materials?	red	red	Yes, electrolysis.
Are there viable alternative processes that would use or generate less harmful materials?	red	red	Yes, electrolysis.
Are there any processes that use or generate materials that are potentially harmful in the supply chain?	red	yellow	CH_4 and CO_2. New CO_2 emissions produced in SMR.
Environmental/Social			
Do your chemical suppliers share your ethical principles?	green	green	Yes, used chemicals bought from ethical corporations.
Social			
Are there any health and safety issues related to harmful nature of chemicals used or generated in the reaction?	yellow	yellow	No specific issues.
Is there deterioration of living environment related to hazardous chemicals generated in the supply chain?	green	green	No, MEA is harmless in lean concentrations.
Economic			
Is there any significant cost related to the harmful nature of the chemicals used or generated in your process?	red	yellow	Yes, CO_2 tax for SMR route.
Green Chemistry Principle 4			Safer chemicals and products
Environmental			
Do the products produced contain harmful or hazardous materials (take into notice also the side products)?	red	green	Yes, CO_2 is a greenhouse gas.
Have you considered your product life cycle according to REACH reporting requirements?	green	green	Chemicals used are registered to REACH.
Have you assessed and examined phases or activities of your product lifecycle (including use and end-of-life phases)?	yellow	yellow	Organic compounds burn always into CO_2 at the end-of-life.
Are there harmful or hazardous chemicals used in the supply chain of the raw materials for your process?	yellow	yellow	Yes, CH_4 as a raw material.
Environmental/Social			
Is there high level of concern associated with the hazardous nature of your products?	yellow	green	Yes, environmental concern on CO_2 emissions of SMR.
Social			
Are there any health and safety issues related to harmful nature of product?	red	red	H_2 and CO are flammable and CO also toxic.
Is there deterioration of living environment related to hazardous chemicals used in the supply chain?	green	green	No dangerous chemicals used in the supply chain.
Is the acceptance of a new product or production process better among society?	yellow	green	Yes (Dry reforming) because of CO_2 usage.
Economic			
Is there any significant cost related to the harmful nature of the chemicals in your product?	yellow	green	CO_2 tax for SMR route.

Green Chemistry Principle 5			Safer solvents and reaction conditions
Environmental			
Do you use solvents and/or other auxiliary chemicals in your processes or products?	green	red	Amine solvent (MEA) in the CO_2 capture.
Are the used solvents considered toxic or hazardous?		yellow	MEA is toxic if swallowed.
Are the solvents used registered within REACH?		green	Yes.
Can you use more benign alternatives?		red	Other separation methods.
Have you considered the number of process units needed in the process and could this be diminished?	green	yellow	Dry reforming has one unit more (CO_2 separation).
Are there toxic or hazardous solvents and/or other auxiliary chemicals used in the supply chain?	green	green	No solvents used in the supply chain.
Social			
Are there any health and safety issues related to harmful nature of solvents, separation agents, or other auxiliary chemicals?		red	MEA is flammable, toxic and corrosive.
Could the more benign alternatives improve the safety?		green	CO_2 separation without toxic solvents.
Is the acceptance of a new product or production process better among society?	yellow	green	Dry reforming because of CO_2 usage.
Economic			
Could the use of more benign alternatives reduce the production cost?		red	MEA separation is the cheapest one.
Could diminishing the number of process units lower the production cost?	red	red	No.
Are the materials needed to construct the process units highly expensive?	yellow	red	Corrosive resistant materials needed in CO_2 separation.
Green Chemistry Principle 6			Energy efficiency
Environmental			
Do your processes require large deviations from ambient temperature and pressure?	yellow	yellow	High temperatures.
Are there suitable alternative processes that operate at ambient or near to ambient temperature and pressure?	red	red	Electrolysis.
Is it possible to develop viable, new processes operating at ambient conditions?	red	red	Electrolysis.
Is all the process energy used for desired material transformation?	yellow	yellow	SMR and DRY considered as ideal cases.
Social			
Are there any health and safety issues related deviation from ambient temperature and pressure?	yellow	yellow	Some health and safety issues related to the high temperatures.
Economic			
How significant is the cost of providing the non-ambient temperature and pressure?	yellow	yellow	Rather significant in both cases.
Could savings be made by operating at ambient temperature and pressure?	red	red	Conversions of raw materials would be too low.
Could the waste heat of the process be utilized somewhere?	green	green	Waste heat is assumed to be utilized.

Green Chemistry Principle 7			Renewable feedstocks
Environmental			
Do you use non-renewable materials in your process?	🟨	🟨	CH$_4$ not renewable.
Can you identify viable and potential candidate materials for substitution from renewable sources (also consider waste materials from recycling streams)?	🟥	🟥	CH$_4$ from biomass sources.
Are these materials readily available?	🟥	🟥	Yes.
Could the use of renewable materials make the product quality better?	🟩	🟩	Not better.
Are there renewable materials used in the supply chain of the raw materials for your process?	🟩	🟩	H$_2$O renewable.
Have you considered the transportation routes of raw materials from source to the plant for each supplier? Have you compared your current supply chain routes to other alternative routes?	🟩	🟩	Similar supply chains.
Environmental/Economic			
Does the use of renewable feedstock involve using different reagents and catalysts? Are they existing, well-studied, perform as well, will their use require more research and involve higher costs?	🟥	🟥	No.
Economic			
Could the use of renewable materials reduce the production cost?	🟥	🟥	No.
Are the process routes studied well enough or is this raising the expenses?	🟩	🟨	SMR more studied.
Is there a possibility to minimize the costs via better logistics planning?	🟩	🟩	No.
Social			
Are there any land use conflicts or deterioration of living environment related to the raw materials?	🟩	🟩	No conflicts.
Green Chemistry Principle 8			Avoiding derivatization
Environmental			
Are there multistage synthetic routes involving blocking and/or protecting groups in your process?	🟩	🟩	No.
Is there additional consumption of materials and energy associated with these stages?	🟩	🟩	No other stages.
Do these stages lead to the generation of additional quantities of unwanted by-products and waste?	🟩	🟩	No other stages.
Can you identify or develop viable alternative routes which don't require the use of blocking and protecting groups?	🟩	🟩	No other stages
Are your raw materials produced by multistage synthetic routes in the supply chain?	🟩	🟩	No.
Social			
Are there any health and safety issues related to the harmful nature of derivatives and temporary modifications?	🟩	🟩	No derivatives.
Economic			
Could the use of these alternative routes reduce the production cost?	🟩	🟩	No derivatives
Is the new process route diminishing the number of process units and thus simplify and lower the cost of the process scheme?	🟩	🟩	No derivatives

Green Chemistry Principle 9			*Catalyst usage*
Environmental			
Does your process use catalyst?	🟩		Both of them use catalysts.
Could the usage of catalytic reactions reduce the generation of undesirable by-products and waste? Increased selectivity?	🟩		Yes.
Would it be easy to add a catalyst into your process?	🟩		Yes.
Would there be material and energy savings achieved by doing this?	🟩		Yes.
Are your raw materials produced by stoichiometric or catalytic routes?	🟩		Catalytic.
Social			
Are there any health and safety issues related to the harmful nature of catalyst material?	🟩		Ni-catalysts are harmless.
Can the use of catalyst make the reaction conditions safer by lowering the temperature and pressure needed?	🟩	🟩	Yes.
Could the need for noble and/or rare earth metals lead to conflicts? Could their use lead to social insecurity?	🟩		Noble metals not used.
Economic			
Could the use of catalyst reduce the production cost e.g. by chancing the type of reactors used, the number of process units and the construction materials?	🟩	🟩	Yes.
Could the use of catalyst reduce the process temperature and pressure and diminish the cost?	🟩		Yes.
Would the use of catalyst result in higher production rate and increase in activity?	🟩		Yes.
Could the catalyst deactivation and ageing cause economic pressures?		🟥	Yes, in dry reforming.
If noble metals are used as catalysts would these cause economic pressures?	🟨		Noble metals not feasible.
Green Chemistry Principle 10			*Degradation of products*
Environmental			
Are your products required to have a long service life and be non degradable?	🟩		No.
Do your products have a high environmental impact at the-end-of life (take into notice also the side products)?	🟥	🟨	CO_2 (negative impact).
Are the products produced persistent at the end-of-life (take into notice also the side products)?	🟨	🟩	CO_2 is.
Is it possible to design new, viable substances/products that degrade at the end of life without compromising the required performance characteristics?	🟥		No.
Social			
Could the more degradable alternatives improve health and safety issues?	🟥		No alternatives.
Economic			
Does the degradability of the products affect the production costs?	🟨	🟩	Yes (CO_2 tax).

Green Chemistry Principle 11			Process monitoring and analysis
Environmental			
Are your chemical processes especially sensitive to process conditions in terms of yields and formation of by-products/selectivity?	🟡	🔴	Dry reforming is more sensitive towards carbon formation.
Would it be easy to introduce real-time reaction monitoring processes?	🟢		Commercial reforming processes have been monitored for a long time.
Social			
Are there any health and safety issues related to changes in process conditions?	🟢		No specific issues.
Economic			
Is there significant cost variations associated with changes in process conditions?	🟡	🔴	Carbon deposits affect more quickly to the efficiency of dry reforming.
Green Chemistry Principle 12			*Minimizing the potential accidents*
Environmental			
Are there hazards related to process (synthetic and formulation activities, involved operations or reaction conditions)?	🟢		No specific hazards.
Is there need to take precautions because of the hazardous nature of the chemicals/conditions to minimise the potential for accidents?	🟡		Normal industrial precautions.
Are there any viable and safer alternatives for the dangerous reaction routes and processes?	🔴		Electrolysis.
Social			
Are there hazards related processes in the supply chain?	🟢		Not in the supply chain.
Do these new alternatives enhance safety performance?	🟢		Yes, because of lower temperatures in electrolysis.
Is there deterioration of living environment related to hazards in the supply chain of the raw materials for your process?	🟡		No differences in the supply chain of the processes.
Economic			
Do the alternatives offer financial savings?	🟢		No, electrolysis is more expensive.

Question	Answer		Explanation
	Syngas	CO2	
Green Chemistry Principle 1			*Waste prevention*
Environmental			
Does the process produce waste?	[green]	[green]	No wastes.
Could this waste be utilised somewhere?	[green]	[green]	No wastes.
Is the waste hazardous?	[green]	[green]	No wastes.
Are there viable process modifications that would produce less waste?	[green]	[green]	No net waste emissions.
Have you considered the amounts of waste produced in the supply chain of the raw materials for your process?	[green]	[green]	Supply chains are simple.
Have you considered the routes of product/by-product and wastes from the production through the end-of-life?	[yellow]	[yellow]	Methanol burns into CO_2.
Social			
Are there any health and safety issues related to the harmful nature of waste?	[green]	[green]	No specific issues.
Economic			
Could there be significant cost related to the treatment and disposal of the waste?	[green]	[green]	No wastes emitted.
Can the waste be used as a valuable side-product?	[green]	[green]	No wastes emitted.
Green Chemistry Principle 2			*Atom economy optimization*
Environmental/Social			
Have you calculated the atom economy for all possible reaction routes and selected the best one?	[green]	[green]	Yes.
Does your synthetic process have high yield?	[green]	[red]	Syngas route yield higher.
Are there better alternative synthetic routes that could be used in the process in terms of yield?			N/A
Social			
Could the alternative reaction route improve the safety of the reaction conditions?			N/A
Are the health impacts minimized?	[yellow]	[green]	CO used in the syngas route.
Economic			
Could the use of these alternative routes reduce the production cost?			N/A
Do all the materials entering the process come out as part of saleable product?	[green]	[red]	CO_2 route produces H_2O.
Have you calculated the atom economy for all possible reactions routes and selected the best one?	[green]	[red]	CO_2 route atom economy is lower.
Does your synthetic process have high yield?	[green]	[red]	Syngas route yield higher.

Green Chemistry Principle 3			Less hazardous syntheses
Environmental			
Does your process use or generate materials that are potentially harmful?	🟩	🟨	CO_2 (consumed).
Are the chemicals used registered within REACH?	🟩	🟩	Yes.
Could there be alternative processes that would use or generate less harmful materials?			N/A
Are there viable alternative processes that would use or generate less harmful materials?			N/A
Are there any processes that use or generate materials that are potentially harmful in the supply chain?	🟩	🟩	No.
Environmental/Social			
Do your chemical suppliers share your ethnical principles?	🟩	🟩	Yes
Social			
Are there any health and safety issues related to harmful nature of chemicals used or generated in the process?	🟥	🟨	Yes (CO and H_2).
Is there deterioration of living environment related to hazardous chemicals generated in the supply chain?	🟩	🟩	No specific deterioration.
Economic			
Is there any significant cost related to the harmful nature of the chemicals used or generated in your process?	🟩	🟩	No specific costs.
Green Chemistry Principle 4			Safer chemicals and products
Environmental			
Do the products produced contain harmful or hazardous materials (take into notice also the side products)?	🟥	🟥	CO, CO_2 and H_2.
Have you considered your product life cycle according to REACH reporting requirements?	🟩	🟩	Chemicals are in REACH.
Have you assessed and examined phases or activities of your product lifecycle (including use and end-of-life phases)?	🟨	🟨	Methanol burns into CO_2.
Are there harmful or hazardous chemicals used in the supply chain of the raw materials for your process?	🟥	🟨	H_2 and CO are flammable.
Environmental/Social			
Is there high level of concern associated with the hazardous nature of your products?	🟩	🟩	No specific concern.
Social			
Are there any health and safety issues related to harmful nature of product?	🟩	🟩	Methanol is safe.
Is there deterioration of living environment related to hazardous chemicals used in the supply chain?	🟨	🟨	No related deterioration.
Is the acceptance of a new product or production process better among society?	🟨	🟩	Yes (CO_2 route).
Economic			
Is there any significant cost related to the harmful nature of the chemicals in your product?	🟩	🟩	No costs.

Green Chemistry Principle 5			Safer solvents and reaction conditions
Environmental			
Do you use solvents and/or other auxiliary chemicals in your processes or products?	green	red	MEA solvent in the CO_2 route.
Are the used solvents considered toxic or hazardous?		yellow	MEA is toxic.
Are the solvents used registered within REACH?		green	Yes.
Can you use more benign alternatives?		red	CO_2 separation with membranes.
Have you considered the number of process units needed in the process and could this be diminished?	green	yellow	CO_2 route has one process unit more.
Are there toxic or hazardous solvents and/or other auxiliary chemicals used in the supply chain?	green	green	No.
Social			
Are there any health and safety issues related to harmful nature of solvents, separation agents, or other auxiliary chemicals?		red	MEA is toxic.
Could the more benign alternatives improve the safety?		red	Yes (no MEA).
Is the acceptance of a new product or production process better among society?	yellow	green	CO_2 route because of CO_2 usage.
Economic			
Could the use of more benign alternatives reduce the production cost?		green	No.
Could diminishing the number of process units lower the production cost?	green	green	No.
Are the materials needed to construct the process units highly expensive?	green	green	No as process conditions are lean.
Green Chemistry Principle 6			Energy efficiency
Environmental			
Do your processes require large deviations from ambient temperature and pressure?	yellow	yellow	Mild deviations are required.
Are there suitable alternative processes that operate at ambient or near to ambient temperature and pressure?			N/A
Is it possible to develop viable, new processes operating at ambient conditions?	green	green	Not possible.
Is all the process energy used for desired material transformation?	green	green	Simulations were ideal cases.
Social			
Are there any health and safety issues related to the deviation from ambient temperature and pressure?	green	green	Lean process conditions.
Economic			
How significant is the cost of providing the non-ambient temperature and pressure?	yellow	yellow	Compression increases costs.
Could savings be made by operating at ambient temperature and pressure?	red	red	Conversion would be too low.
Could the waste heat of the process be utilized somewhere?	green	green	Yes.

Green Chemistry Principle 7			Renewable feedstock utilization
Environmental			
Do you use non-renewable materials in your process?	🟥	🟥	Syngas.
Can you identify viable and potential candidate materials for substitution from renewable sources?	🟥	🟥	Yes, biomass.
Are these materials readily available?	🟥	🟥	Yes.
Could the use of renewable materials make the product quality better?	🟩	🟩	No.
Are there renewable materials used in the supply chain of the raw materials for your process?	🟩	🟩	Water is renewable.
Have you considered the transportation routes of raw materials from source to the plant for each supplier? Have you compared your current supply chain routes to other alternative routes?	🟩	🟩	On-site piping.
Environmental/Economic			
Does the use of renewable feedstock involve using different reagents and catalysts? Are they existing, well-studied, perform as well, will their use require more research and involve higher costs?	🟩	🟩	Same reagents and catalysts.
Economic			
Could the use of renewable materials reduce the production cost?	🟥	🟥	No.
Are the process routes studied well enough or is this raising the expenses?		🟨	CO_2 route needs more research.
Is there a possibility to minimize the costs via better logistics planning?	🟩	🟩	Logistics are optimized.
Social			
Are there any land use conflicts or deterioration of living environment related to the raw materials?	🟩	🟩	No (on-site piping).
Green Chemistry Principle 8			Avoiding unneccessary derivatization
Environmental			
Are there multistage synthetic routes involving blocking and/or protecting groups in your process?	🟩	🟩	No synthetic stages.
Is there additional consumption of materials and energy associated with these stages?	🟩	🟩	No synthetic stages.
Do these stages lead to the generation of additional quantities of unwanted by-products and waste?	🟩	🟩	No synthetic stages.
Can you identify or develop viable alternative routes which don't require the use of blocking and protecting groups?	🟩	🟩	No synthetic stages.
Are your raw materials produced by multistage synthetic routes in the supply chain?	🟩	🟩	No.
Social			
Are there any health and safety issues related to the harmful nature of derivatives and temporary modifications?	🟩	🟩	No derivatives.
Economic			
Could the use of these alternative routes reduce the production cost?	🟩	🟩	No.
Is the new process route diminishing the number of process units and thus simplify and lower the cost of the process scheme?	🟩	🟩	No.

Green Chemistry Principle 9			Catalyst usage
Environmental			
Does your process use catalyst?	🟩	🟩	Yes.
Could the usage of catalytic reactions reduce the generation of undesirable by-products and waste? Increased selectivity?	🟩	🟩	Yes.

Question			Answer
Would it be easy to add a catalyst into your process?	🟩	🟩	Yes.
Would there be material and energy savings achieved by doing this?	🟩	🟩	Yes.
Are your raw materials produced by stoichiometric or catalytic routes?	🟩	🟩	Yes.
Social			
Are there any health and safety issues related to the harmful nature of catalyst material?	🟩	🟩	No.
Can the use of catalyst make the reaction conditions safer by lowering the temperature and pressure needed?	🟩	🟩	Yes.
Could the need for noble and/or rare earth metals lead to conflicts? Could their use lead to social insecurity?	🟩	🟩	Used metals are not rare.
Economic			
Could the use of catalyst reduce the production cost e.g. by chancing the type of reactors used, the number of process units and the construction materials?	🟩	🟩	Yes.
Could the use of catalyst reduce the process temperature and pressure and diminish the cost?	🟩	🟩	Yes.
Would the use of catalyst result in higher production rate and increase in activity?	🟩	🟩	Yes.
Could the catalyst deactivation and ageing cause economic pressures?	🟩		Service life 2-5 years.
If noble metals are used as catalysts would these cause economic pressures?	🟩		Noble metals not suitable.
Green Chemistry Principle 10			*Degradation of products*
Environmental			
Are your products required to have a long service life and be non degradable?	🟩	🟩	No.
Do your products have a high environmental impact at the-end-of life (take into notice also the side products)?	🟥	🟥	End product is CO_2.
Are the products produced persistent at the end-of-life (take into notice also the side products)?	🟩	🟩	No.
Is it possible to design new, viable substances/products that degrade at the end of life without compromising the required performance characteristics?	🟥	🟥	Not possible.
Social			
Could the more degradable alternatives improve health and safety issues?			No alternatives.
Economic			
Does the degradability of the products affect the production costs?	🟩	🟩	No.

Green Chemistry Principle 11			Process monitoring and analysis
Environmental			
Are your chemical processes especially sensitive to process conditions in terms of yields and formation of by-products/selectivity?			Temperature sensitive because of catalysts.
Would it be easy to introduce real-time reaction monitoring processes?			Yes (mild process conditions).
Social			
Are there any health and safety issues related to changes in process conditions?			No specific issues.
Economic			
Is there significant cost variations associated with changes in process conditions?			No significant cost variations.
Green Chemistry Principle 12			Minimizing the potential accidents
Environmental			
Are there hazards related to process (synthetic and formulation activities, involved operations or reaction conditions)?			No specific hazards.
Is there need to take precautions because of the hazardous nature of the chemicals/conditions to minimise the potential for accidents?			No specific precautions needed.
Are there any viable and safer alternatives for the dangerous reaction routes and processes?			No alternatives.
Social			
Are there hazards related processes in the supply chain?			No specific hazards.
Do these new alternatives enhance safety performance?			No alternatives.
Is there deterioration of living environment related to hazards in the supply chain of the raw materials for your process?			Not related.
Economic			
Do the alternatives offer financial savings?			No alternatives.

Question	Ans wer		Explanation
	OXY	**CO2**	
Green Chemistry Principle 1			*Waste prevention*
Environmental			
Does the process produce waste?	red	green	Carbonylation does (CO_2).
Could this waste be utilised somewhere?	yellow	green	Not without energy input.
Is the waste hazardous?	red	green	CO_2 is a greenhouse gas.
Are there viable process modifications that would produce less waste?			N/A
Have you considered the amounts of waste produced in the supply chain of the raw materials for your process?	green	green	Raw materials come straight from a pipe.
Have you considered the routes of product/by-product and wastes from the production through the end-of-life?	yellow	yellow	DMC is used in a chemical synthesis.
Social			
Are there any health and safety issues related to the harmful nature of waste?	green	green	CO_2 is safe to humans.
Economic			
Could there be significant cost related to the treatment and disposal of the waste?	red	green	CO_2 tax.
Can the waste be used as a valuable side-product?	yellow	green	Not without energy input.
Green Chemistry Principle 2			*Atom economy optimization*
Environmental/Social			
Have you calculated the atom economy for all possible reaction routes and selected the best one?	green	yellow	89.4 % (carbonylation) vs. 83.3 % (CO_2 route)
Does your synthetic process have high yield?	red	red	Yield of DMC is low.
Are there better alternative synthetic routes that could be used in the process in terms of yield?	red	red	Yes, phosgene route gives better yields for DMC.
Social			
Could the alternative reaction route improve the safety of the reaction conditions?	red	red	Phosgenation is a dangerous process.
Are the health impacts minimized?	yellow	green	CO as raw material more dangerous than CO_2.
Economic			
Could the use of these alternative routes reduce the production cost?	green	green	DMC yield would be higher.
Do all the materials entering the process come out as part of saleable product?	red	red	Yield of DMC is low in both routes.
Have you calculated the atom economy for all possible reactions routes and selected the best one?	green	yellow	89.4 % (carbonylation) vs. 83.3 % (CO_2 route).
Does your synthetic process have high yield?	red	red	Yield of DMC is low.

Green Chemistry Principle 3			Less hazardous syntheses
Environmental			
Does your process use or generate materials that are potentially harmful?	🟥	🟩	Carbonylation produces CO_2.
Are the chemicals used registered within REACH?	🟩		Yes.
Could there be alternative processes that would use or generate less harmful materials?	🟩		Phosgenation (uses harmful chemicals).
Are there viable alternative processes that would use or generate less harmful materials?	🟩		Phosgenation is more harmful.
Are there any processes that use or generate materials that are potentially harmful in the supply chain?	🟩		No specific processes.
Environmental/Social			
Do your chemical suppliers share your ethnical principles?	🟩		Yes.
Social			
Are there any health and safety issues related to harmful nature of chemicals used or generated in the process?	🟥		CO and MEA are toxic.
Is there deterioration of living environment related to hazardous chemicals generated in the supply chain?	🟩		No deterioration related.
Economic			
Is there any significant cost related to the harmful nature of the chemicals used or generated in your process?	🟥	🟩	CO_2 tax costs.
Green Chemistry Principle 4			Safer chemicals and products
Environmental			
Do the products produced contain harmful or hazardous materials (take into notice also the side products)?	🟥	🟥	CO_2.
Have you considered your product life cycle according to REACH reporting requirements?	🟩		All chemicals used belong to REACH.
Have you assessed and examined phases or activities of your product lifecycle (including use and end-of-life phases)?	🟩		DMC used in chemical synthesis.
Are there harmful or hazardous chemicals used in the supply chain of the raw materials for your process?	🟨		Methane (GHG) to produce methanol.
Environmental/Social			
Is there high level of concern associated with the hazardous nature of your products?	🟥	🟨	Environmental concern on CO_2 emissions.
Social			
Are there any health and safety issues related to harmful nature of product?	🟩		No health and safety issues.
Is there deterioration of living environment related to hazardous chemicals used in the supply chain?	🟩		No specific relation.
Is the acceptance of a new product or production process better among society?	🟨	🟩	CO_2 route because of CO_2 usage.
Economic			
Is there any significant cost related to the harmful nature of the chemicals in your product?	🟥	🟩	CO_2 tax costs.

Green Chemistry Principle 5			Safer solvents and reaction conditions
Environmental			
Do you use solvents and/or other auxiliary chemicals in your processes or products?	green	red	MEA solvent in the CO_2 utilizing process.
Are the used solvents considered toxic or hazardous?		yellow	MEA is toxic but not very hazardous.
Are the solvents used registered within REACH?		green	Yes.
Can you use more benign alternatives?		red	CO_2 separation with membranes.
Have you considered the number of process units needed in the process and could this be diminished?	green	yellow	CO_2 route needs one process unit more.
Are there toxic or hazardous solvents and/or other auxiliary chemicals used in the supply chain?	green	green	No.
Social			
Are there any health and safety issues related to harmful nature of solvents, separation agents, or other auxiliary chemicals?		red	MEA is toxic.
Could the more benign alternatives improve the safety?	red	red	Membrane separation would be safer.
Is the acceptance of a new product or production process better among society?	yellow	green	CO_2 route because of CO_2 usage.
Economic			
Could the use of more benign alternatives reduce the production cost?	red	red	Membrane separation is more expensive.
Could diminishing the number of process units lower the production cost?	yellow	yellow	No.
Are the materials needed to construct the process units highly expensive?	green	green	No because of mild process conditions.
Green Chemistry Principle 6			Energy efficiency
Environmental			
Do your processes require large deviations from ambient temperature and pressure?	green	green	Rather atmospheric conditions.
Are there suitable alternative processes that operate at ambient or near to ambient temperature and pressure?	yellow	yellow	Phosgenation works at ambient conditions.
Is it possible to develop viable, new processes operating at ambient conditions?	green	green	Already at ambient conditions.
Is all the process energy used for desired material transformation?	green	green	Simulations were ideal cases.
Social			
Are there any health and safety issues related to the deviation from ambient temperature and pressure?	green	green	No health and safety issues.
Economic			
How significant is the cost of providing the non-ambient temperature and pressure?	green	green	No costs.
Could savings be made by operating at ambient temperature and pressure?	green	green	Conversions would be too low.
Could the waste heat of the process be utilized somewhere?	green	green	Assumed is that yes.

Green Chemistry Principle 7			Renewable feedstocks
Environmental			
Do you use non-renewable materials in your process?	🟥		Yes.
Can you identify viable and potential candidate materials for substitution from renewable sources (also consider waste materials from recycling streams)?	🟩	🟩	No.
Are these materials readily available?			N/A
Could the use of renewable materials make the product quality better?	🟩	🟩	No.
Are there renewable materials used in the supply chain of the raw materials for your process?	🟩	🟩	Water.
Have you considered the transportation routes of raw materials from source to the plant for each supplier? Have you compared your current supply chain routes to other alternative routes?	🟩		Supply chain is optimized.
Environmental/Economic			
Does the use of renewable feedstock involve using different reagents and catalysts? Are they existing, well-studied, perform as well, will their use require more research and involve higher costs?			N/A
Economic			
Could the use of renewable materials reduce the production cost?	🟥		N/A
Are the process routes studied well enough or is this raising the expenses?	🟩	🟥	CO_2 route not.
Is there a possibility to minimize the costs via better logistics planning?	🟩		Logistics optimized.
Social			
Are there any land use conflicts or deterioration of living environment related to the raw materials?	🟩	🟩	Not related.
Green Chemistry Principle 8			Avoiding derivatization
Environmental			
Are there multistage synthetic routes involving blocking and/or protecting groups in your process?	🟩		No.
Is there additional consumption of materials and energy associated with these stages?	🟩		No.
Do these stages lead to the generation of additional quantities of unwanted by-products and waste?	🟩		No.
Can you identify or develop viable alternative routes which don't require the use of blocking and protecting groups?	🟩		Not required.
Are your raw materials produced by multistage synthetic routes in the supply chain?	🟩		No.
Social			
Are there any health and safety issues related to the harmful nature of derivatives and temporary modifications?	🟩	🟩	No.
Economic			
Could the use of these alternative routes reduce the production cost?	🟥	🟥	
Is the new process route diminishing the number of process units and thus simplify and lower the cost of the process scheme?	🟩		No.

Green Chemistry Principle 9			Catalyst usage
Environmental			
Does your process use catalyst?	🟩		Both of them.
Could the usage of catalytic reactions reduce the generation of undesirable by-products and waste? Increased selectivity?	🟩		Yes.
Would it be easy to add a catalyst into your process?	🟩		Yes.
Would there be material and energy savings achieved by doing this?	🟩		Yes.
Are your raw materials produced by stoichiometric or catalytic routes?	🟩		Yes.
Social			
Are there any health and safety issues related to the harmful nature of catalyst material?	🟩		No harmful materials.
Can the use of catalyst make the reaction conditions safer by lowering the temperature and pressure needed?	🟩		Yes.
Could the need for noble and/or rare earth metals lead to conflicts? Could their use lead to social insecurity?	🟩		No.
Economic			
Could the use of catalyst reduce the production cost e.g. by chancing the type of reactors used, the number of process units and the construction materials?	🟩		Yes.
Could the use of catalyst reduce the process temperature and pressure and diminish the cost?	🟩		Yes.
Would the use of catalyst result in higher production rate and increase in activity?	🟩		Yes.
Could the catalyst deactivation and ageing cause economic pressures?	🟨		Catalysts rather cheap.
If noble metals are used as catalysts would these cause economic pressures?	🟨		Noble metals not feasible.
Green Chemistry Principle 10			Degradation of products
Environmental			
Are your products required to have a long service life and be non degradable?	🟩		Not required.
Do your products have a high environmental impact at the-end-of life (take into notice also the side products)?	🟥		CO_2 of carbonylation.
Are the products produced persistent at the end-of-life (take into notice also the side products)?	🟩		DMC is persistent.
Is it possible to design new, viable substances/products that degrade at the end of life without compromising the required performance characteristics?	🟥		Not possible.
Social			
Could the more degradable alternatives improve health and safety issues?	🟩		Phosgenation does not improve health and safety issues.
Economic			
Does the degradability of the products affect the production costs?	🟩		No.

Green Chemistry Principle 11			Process monitoring and analysis
Environmental			
Are your chemical processes especially sensitive to process conditions in terms of yields and formation of by-products/selectivity?			Not very sensitive.
Would it be easy to introduce real-time reaction monitoring processes?			Low temperature and pressure so monitoring won't cause problems.
Social			
Are there any health and safety issues related to changes in process conditions?			No specific issues.
Economic			
Is there significant cost variations associated with changes in process conditions?			No significant cost variations.
Green Chemistry Principle 12			*Minimizing the potential accidents*
Environmental			
Are there hazards related to process (synthetic and formulation activities, involved operations or reaction conditions)?			No specific hazards.
Is there need to take precautions because of the hazardous nature of the chemicals/conditions to minimise the potential for accidents?			No specific precautions needed.
Are there any viable and safer alternatives for the dangerous reaction routes and processes?			Phosgenation is more dangerous.
Social			
Are there hazards related processes in the supply chain?			No.
Do these new alternatives enhance safety performance?			Phosgenation makes safety performance worse.
Is there deterioration of living environment related to hazards in the supply chain of the raw materials for your process?			CH_4 and CO_2 emissions.
Economic			
Do the alternatives offer financial savings?			Phosgenation gives better yield of DMC.